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Extent of Denitrification in Northport Groundwater

A Thesis Presented By

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In partial fulfillment of the requirements for the degree

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Abstract of the Thesis

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Long Island drinking water is provided by a sole source aquifer with nitrate levels exceeding the federal limit of 10ppm in some communities. Previous studies undertaken in the community of Northport identified a 50% loss of nitrogen in the system (MUNSTER, 2004; MUNSTER, 2008). A study of ^{15}N- NO_3^- and ^{18}O-NO_3^- identified sewage and fertilizer applications as the primary nitrogen contaminators in Northport (BLEIFUSS et al., 2000) but did not conclusively find evidence

of denitrification or ammonia volatilization in the isotope signature. No study to date has been able to identify the mechanism for 50% nitrogen loss within the system.

Groundwater denitrification was investigated as the mechanism for calculated 50% nitrogen deficit in a Long Island's coastal plain aquifer. Samples were taken from municipal supply wells and monitoring wells during May and October of 2008. Groundwater analysis included major ions, dissolved oxygen, dissolved organic carbon and dissolved N_2/Ar ratios. Anion concentrations were used to estimate nitrogen inputs from three primary sources; on site wastewater disposal systems, fertilizer applications and atmospheric deposition. Field measured dissolved oxygen concentrations were used to identify hypoxic conditions that favor denitrification. Dissolved organic carbon was measured to categorize if sufficient electron donors exist to drive the denitrification reaction. Dissolved N_2/Ar gases were measured using membrane inlet mass spectrometry (MIMS) to quantify excess N_2 produced *via* denitrification.

Dissolved oxygen concentrations exceed 4mg/l in all municipal supply samples and four of five monitoring well samples. Dissolved organic carbon concentrations are less than 0.5mg-C/l in municipal supply well samples. Nitrate ($N-NO_3^-$) denitrified is less than 2ppm for all samples. Samples with high dissolved oxygen concentration contain nitrate ranging from 2.0 – 11.0mg/l $N-NO_3^-$.

We hypothesize thick vadose zone keeps dissolved oxygen content close to saturation during groundwater infiltration. Travel time from groundwater infiltration to well production is short, less than 50 years for municipal supply wells, which prevents typical age related oxygen depletion within the aquifer. A combination of thick vadose zone and short groundwater travel

time oxidizes residual cesspool ammonium and dissolved organic carbon, eliminating electron

donors that fuel denitrification. High dissolved oxygen concentrations in groundwater prevent

saturated zone denitrification. We conclude that groundwater denitrification cannot account

for observed 50% nitrogen loss in Northport, Long Island.

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Introduction

Suffolk County, NY has a sole source aquifer serving over one million people. Groundwater in Suffolk County is pumped from two large connected sandy aquifers, the Pleistocene Upper Glacial Aquifer and the Cretaceous Magothy Aquifer. Nitrate contamination is a major concern for both aquifers as 70% of Suffolk County homes rely on septic tank/cesspool systems that discharge directly to the groundwater. Most of the water from the aquifers is discharged to the surrounding seawater by submarine groundwater discharge; a minor amount reaches the seawater through streams. In Suffolk County submarine groundwater discharge (SGD) contributes to the eutrophication of Long Island Sound (BOKUNIEWICZ et al., 2003). Nitrate contamination due to urban pollutants is observed and studied worldwide (HUA et al., 2009) but studies of natural attenuation of nitrate is underrepresented in the literature (SEITZINGER et al., 2006). This research is directed at evaluating the extent of denitrification at a particular site on representative of much of the aquifer on Long Island. The purpose of the study reported here is to determine if aquifer denitrification can account for significant nitrogen lost in the groundwater flow system of Northport, Long Island.

Study Area

We chose Northport as our study area for three reasons. First, Northport has nitrate concentrations in excess of 10ppm, the federal drinking water limit. Second, Northport underwent extensive suburban development with the use of septic tanks for sewage treatment rather than sewage treatment plants. This is typical of Suffolk County development where septic tanks are used in 70% of the homes. Finally, nitrogen loading to Northport groundwater has been extensively studied (MUNSTER, 2004); (MUNSTER, 2008); (BLEIFUSS et al., 2000)but nitrogen loss mechanisms are poorly quantified. With the selection of Northport for our denitrification study site we hope to produce relevant field data for application within existing nitrogen models like WBLMER.

The stratigraphy along the North Shore of Long Island is characterized by unconsolidated Cretaceous alluvial and deltaic sediments and overlying Pleistocene glacial deposits on a

crystalline bedrock surface, dipping 1° to the southeast (CAMP et al., 2005). In Northport the Pleistocene glacial deposits form the Upper Glacial aquifer extending from ground surface to a maximum of 250 feet below sea level. The Upper Glacial aquifer consists of poorly sorted medium- to coarse-grained quartz rich sands and gravel. In places the Upper Glacial deposits are inter-bedded with Smithtown clay consisting of tan silty clay (CAMP et al., 2005). The Upper Glacial aquifer is underlain by the Magothy Aquifer which is characterized by fine, silty gray sand.

Groundwater flow in the Northport region is north-northeast with groundwater recharge predominantly happening along the central long axis of Long Island and groundwater flowing north and south to discharge into Long Island Sound and the Atlantic Ocean, respectively. Recharge from precipitation is approximately 56cm/year (BUSCIOLANO, 2004). Due to evapotranspiration of precipitation during summer months, primary groundwater recharge in Northport happens during the period from October to March (STEENHUIS et al., 1985).

Groundwater in Northport flows toward the Sunken Meadow drainage system and Long Island Sound. Previous studies have calculated the average downward hydraulic head gradient of 0.0035 (CAMP et al., 2005). The ratio of vertical to horizontal hydraulic conductivity in the Upper Glacial Aquifer ranges from 1:10 to 1:24. Given this large ratio, catchment areas for the Northport wells tend to be teardrop shaped, growing larger as they extend south from the well to the center of Long Island.

Monti and Busciolano (2009) used water level measurements from 502 wells across Long Island in March-April of 2006 to create a water table and potentiometric surface map of the Upper Glacial, Magothy and Lloyd aquifers. Capture zones for supply wells overlap due to long screen lengths and well depths in excess of 250 feet. Vadose zone thickness for combined capture zone derived from water table elevation data shows a general trend of thickening from north to south. In the study area average vadose zone thickness ranges from 71 to 157 ft. South of the study area, where water for Northport municipal supply wells is recharged, vadose zone thickness increases to a maximum of 249 feet (MONTI and BUSCIOLANO, 2009).

Figure 1 shows a map of municipal supply well locations and monitoring well locations tested in this study. Major roads and towns are given for reference. Water table contours from (MONTI and BUSCIOLANO, 2009).
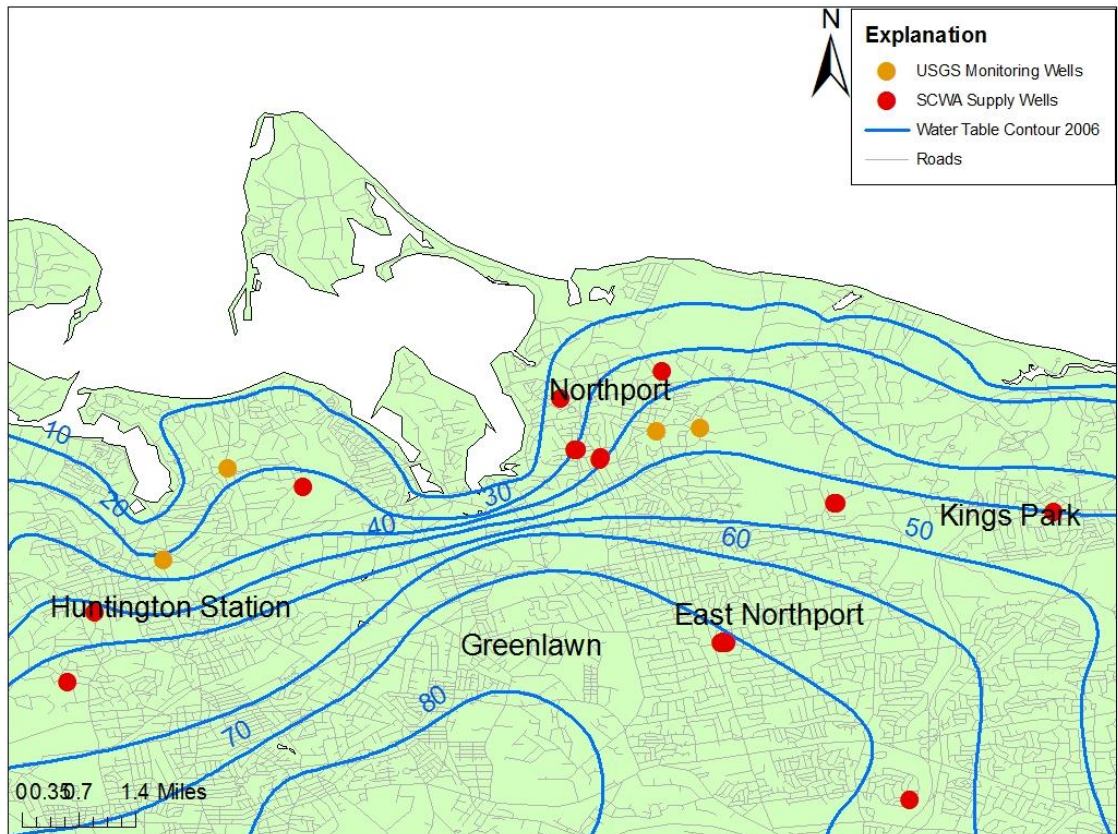
Figure 1 Map of study area. Water table contours are from USGS water level monitoring network (MONTI and BUSCIOLANO, 2009). Samples were taken from monitoring wells, shown in yellow, municipal supply wells shown in red. Towns and major roads are shown for reference.

In Suffolk County, groundwater nitrate concentrations in excess of 10 mgL^{-1} have been found in Northport on the North Fork of Long Island. The federal regulatory limit for nitrate in drinking water is 10mgL^{-1}. This limit is based on evidence that infants are susceptible to methemoglobinemia if fed formula or other products mixed with water containing more than

$10 mgL^{-1}$ nitrate. In Infant digestive system nitrate (NO_3^-) is reduced to nitrite (NO_2^-) which then binds to hemoglobin and is converted to methemoglobin which decreases the oxygen carrying capacity of blood. The U.S EPA does not classify nitrate as a human carcinogen(AGENCY, 2009) due to insufficient data in human testing. Recent studies suggest a link between long term consumption of drinking water with elevated nitrate levels and increased incidence of Non-Hodgkin's Lymphoma (WARD et al., 1996); (CHIU et al., 2008).

Nitrogen Inputs

The major sources for nitrate in groundwater in Northport are: atmospheric deposition, fertilizer applications and on site wastewater disposal systems (MUNSTER, 2004). Until the 1950's Northport was dominantly a farming community with agricultural fertilizers contributing the bulk of nitrate contamination. According to Bleifuss (2000) nitrogen loading according to agricultural land use averages $8.6 – 9.6$ mgL^{-1} $N-NO_3^-$. These values approach the 10 mgL^{-1} maximum contamination level for drinking.   The residence time in the Upper Glacial aquifer in Northport is less than 50 years so it is believed that agricultural derived nitrate contamination is no longer a factor (BUXTON and MODICA, 1992). During the 1950s and 1960s the Northport area shifted from agricultural to medium density housing, defined as 2-4 housing units/acre (KOPPELMAN, 1978).

By the late 1950s most of the land in Northport had been converted to private residences with septic tank-cesspool systems. Population increase had the effect of increasing nitrate contamination to the groundwater via sewage effluent. Bleifuss (2000) used oxygen isotope composition in nitrate to show that chemical fertilizers from earlier agricultural practices no longer affect Northport water quality. Additionally, based on anion and cation concentrations in groundwater, Munster (2004) concluded that in Northport up to 50% of water recharging the Upper Glacial aquifer is derived from sewage,.

Precipitation

Nitrate deposition via precipitation is the smallest contributor to groundwater nitrate pollution. The National Atmospheric Deposition Program/NTN records nitrogen concentrations in precipitation at site NY96, Cedar Beach in Southold, NY. Data is given as weighted mean

concentration of seasonal precipitation. For the year 2008-2009 NH_4^+ concentration was 0.146mg/l. During that same period NO_3^- concentration was 0.820mg/l (PROGRAM/NTN, 2008).

Fertilizer applications

Koppelman (1978) classified 25% of Suffolk county land as lawns. The town of Huntington has a fertilizer application rate of 66kg/acre/year, which is 50% higher than other towns on Long Island. Annual precipitation on Long Island averages 112.2cm per year (BUSCIOLANO, 2004) with approximately 50% recharged to groundwater. Additionally, Suffolk county Water Authority (SCWA) provides an estimated 73 billion liters of water for irrigation purposes. Therefore, groundwater recharged via fertilized applications on turfgrass plots is a key component in nitrate loading to groundwater in the community of Northport.

Munster (2008) found that soilwater collected at a depth of 150cm beneath chemically and organically fertilized turfgrass plots has a 25% chance of containing NO_3^- concentrations greater than the 10 mgL^{-1} federal drinking water standard. This study calculated excess nitrogen beyond uptake by plants and retention in the soil. Figure 2 shows that soilwater collected beneath chemically and organically fertilized turfgrass plots contained greater than 5mgL^{-1} N- NO_3^- during the months of October to March, which coincides with the months of greatest groundwater recharge (STEENHUIS et al., 1985).
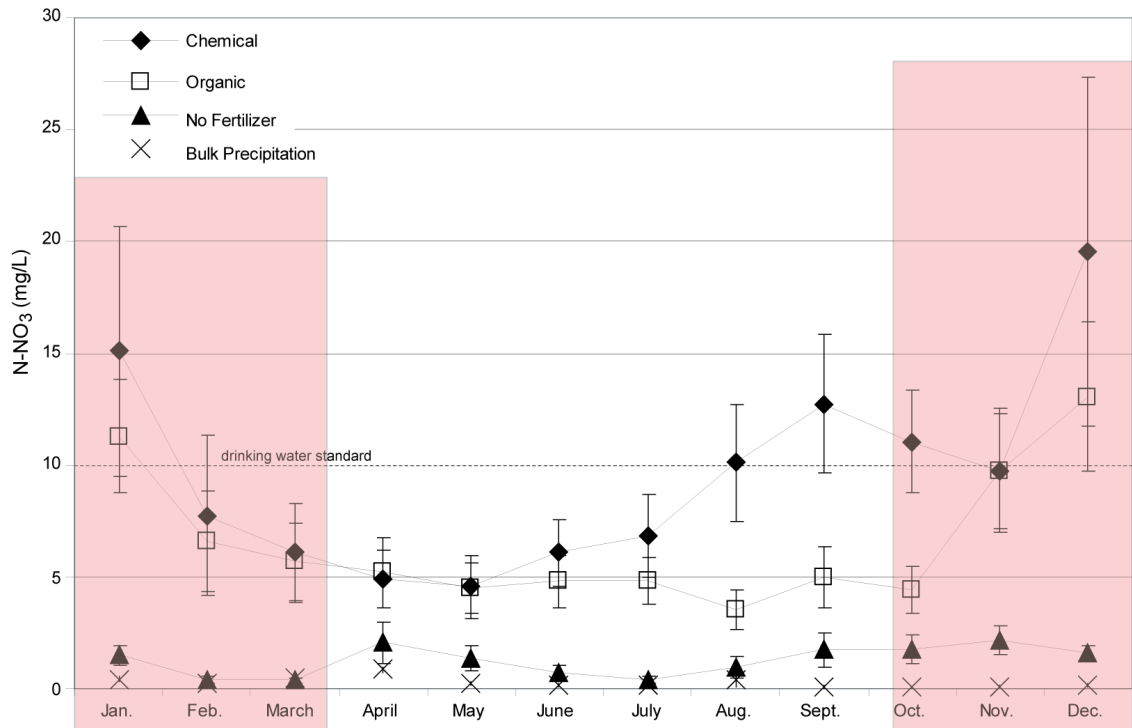
Figure 2 Monthly average N-NO3 concentrations of soil water collected at 100 cm from the combined years 2003- 2006, and for bulk precipitation collected from May 2005 to January 2007. Error bars are standard error of the mean. The EPA drinking water standard is 10 mg/L, represented by the dashed horizontal line. Shaded areas highlight elevated nitrate concentrations in soil water during months of greatest groundwater recharge. Modified from **(MUNSTER, 2008).**

On Site Wastewater Disposal systems

70% of homes in Suffolk County use on site wastewater disposal systems. In Northport the large number of septic wastewater disposal systems dramatically increased groundwater nitrate contamination in the last fifty years. A four person home discharges sewage with between 27.1 ppm and 64.3 mgL^{-1} nitrogen (MUNSTER, 2008). The nitrogen in sewage entering the septic tank is dissolved organic nitrogen (DON) and ammonium (NH$_4^+$) the nitrogen is dominantly ammonium when it leaves the cesspool. Porter (1980) suggests a 20% loss of nitrogen during transport from septic tank to cesspool, most likely due to ammonia gas volatilization. Sediments surrounding the cesspool are highly aerated and well drained, which favors nitrification of

remaining nitrogen. If we assume that all remaining nitrogen oxidizes to nitrate, then 80% of annual septic discharge per home is recharged with groundwater, 21.7mgL^{-1} - 51.4 mgL^{-1} N-NO$_3^-$. Even if only 50% of annual septic discharge per home is oxidized to nitrate, on site disposal systems are still the primary contributors to groundwater nitrate pollution.

Munster (2004) calculated expected nitrate concentration for Northport supply wells based on land use in the catchment area. This analysis showed that the groundwater in Northport contained 50% less nitrate than would be expected. Valiela et al. (1997) designed the Waquoit Bay Land Margin Ecosystems Research (WBLMER) model now widely used to calculate nitrogen loading to surface bodies in coastal plain sediments like those in Cape Cod, MA and Long Island, NY. This model characterizes nitrogen loss as point and non-point. Atmospheric deposition and fertilizer applications sources are considered non-point or 'diffuse' sources of nitrogen. WBLMER allows for 61% loss of diffuse nitrogen within the vadose zone and 35% loss of diffuse nitrogen in the aquifer, based on mass balance calibrations beneath a forested parcel of land. WBLMER classifies on site wastewater disposal systems as point source nitrogen loss and suggests a 40% nitrogen loss from this source.

Nitrogen loss in groundwater is thought to occur via one of four mechanisms; ammonia volatilization, ammonium sorption onto sediments, vadose zone denitrification and groundwater denitrification (VALIELA et al., 1997). In this study we investigate the possibility that denitrification in groundwater could account for nitrogen loss in Northport.

Denitrification Background

Removal of nitrate from groundwater *via* artificial means is costly and time consuming. Typical methods include permeable reactive barrier that use Fe^0 to reduce nitrate to nitrogen gas or ammonium, membrane attached biofilms with supplemental carbon source and use of immobilized enzymes in denitrification reactors (SHRIMALI and SINGH, 2001). The expense of denitrification for municipal water supply makes the understanding of natural denitrification crucial to local water suppliers.

Denitrification is the microbially mediated reduction of nitrate (NO_3^-) to nitrogen gas (N_2). The generalized half reaction for all denitrification reactions is:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad\qquad 1$$
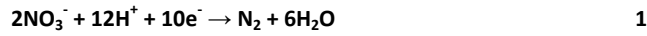
Four requirements must be met for denitrification to occur (KOROM and HX, 1992).

i.   Presence of NO_3^- to act as terminal electron acceptor

ii.   Hypoxic or anoxic conditions

iii. Bacteria to perform the stepwise reduction of nitrate to nitrogen gas.

     a. $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

iv.   Electron donors to fuel either organotrophic or lithotrophic bacteria performing denitrification

Aquifers contain chemotrophic bacteria that oxidize either organic or inorganic compounds for energy. Organotrophic bacteria use organic electron donors to fuel cellular functions. Litotrophs use inorganic electron donors, including carbon dioxide, as fuel (KOROM and HX, 1992).

The majority of denitrifying bacteria are heterotrophic facultative anaerobes (PAYNE, 1981). They are capable of survival with or without oxygen and will utilize organic carbon in the most energetically favorable reaction possible. The most common electron acceptors in groundwater are oxygen and nitrate. The change in Gibbs free energy for oxygen use is slightly higher than for nitrate use. Bacteria prefer the more abundant and energetically favorable oxygen for metabolism.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \Delta G = - 2870 \text{ kJ/mol (STROHM et al., 2007)} \qquad (2)$$

$$5\,C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 12N_2 + 30CO_2 + 42H_2O \quad \Delta G = -2670 \text{ kJ/mol (STROHM et al., 2007)} \qquad (3)$$
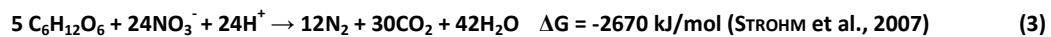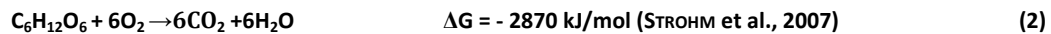
It is believed that dissolved oxygen concentration in groundwater and depth below the water table are inversely proportional (KOROM and HX, 1992);(SOARES and FH, 2000). Northport supply wells are screened for long intervals between 170 and 480 ft below water table. We expected to find denitrification in Northport public supply wells and in deeper monitoring wells if electron donors are present as dissolved oxygen should be depleted at depth (GILLHAM and CHERRY, 1978).

Denitrifying bacteria are present throughout the sedimentary column (KOROM and HX, 1992). In systems with anoxic conditions the limiting factor in groundwater denitrification is electron donor concentration. Denitrifying bacteria can be either organotrophic or lithotrophic. Lithotrophic bacteria rely on reduced minerals to denitrify, typically Fe^{2+}, Mn^{2+} (KOROM and HX, 1992).

Membrane Inlet Mass Spectrometry

Many techniques are available for determining the extent of denitrification (SEITZINGER et al., 2006). These include acetylene inhibition (ADDY et al., 1999), nitrogen and oxygen isotope values for dissolved nitrate (ARAVENA and ROBERTSON, 1998), dissolved N_2/Ar ratios (BLICHER-MATHIESEN et al., 1998) or a combination of these techniques (SCHURMANN et al., 2003). We chose to use dissolved N_2/Ar ratios as determined by membrane inlet mass spectrometry (MIMS) to quantify denitrification in Northport wells for the following reasons.

- N_2 is the direct byproduct of denitrification which eliminates error incurred by measuring proxy byproducts such as N_2O (acetylene inhibition) or ^{15}N (isotope enrichment).
- Samples for N_2/Ar measurement can be collected from both public supply and monitoring wells as they don't require injection of any substance into the well
- MIMS analysis allows small sample size (<10ml) and eliminates the degassing step which typically introduces the largest percentage of analysis error for other methods of measuring the N_2/Ar ratios (KANA et al., 1994).
- MIMS coefficient of variation is less than 0.5% for N_2 and Ar concentrations across a wide range of temperature equilibrations (KANA et al., 1994).

- o Coefficient of variation is defined as the ratio of the standard deviation to the mean $C_v = \sigma/\mu$, where μ is the mean of replicate samples injections and σ is the standard deviation.

Methods

Groundwater from public supply wells in Northport was analyzed for denitrification using direct measurement of excess nitrogen gas to argon ratios via MIMS. The same groundwater samples were analyzed for dissolved organic carbon, cations, anions, nitrate and dissolved oxygen to characterize sources and redox conditions in Northport groundwater. Excess nitrogen gas concentrations were considered relative to the nitrogen isotope data from Bleifuss (2000) to evaluate the possibility of vadose zone denitrification.   Finally, a conceptual model is presented to explain the effect of vadose zone thickness on groundwater denitrification in Northport samples.

Membrane Inlet Mass Spectrometry

Previous studies have used Membrane Inlet Mass Spectrometry to determine N_2 and Ar concentrations in water with high precision (SINGLETON et al., 2007);(KROEGER et al., 2006). This method has the advantage of eliminating the degassing step so dissolved gases are measured in line with the mass spectrometer. Samples were analyzed by Kevin Kroeger of U.S Geological Survey Woods Hole science Center using Anne Giblin's mass spectrometer laboratory at the Marine Biological Laboratory in Woods Hole, MA using procedures developed by Kana (KANA et al., 1994). Calibration standards are water equilibrated with air at a known temperature, salinity and pressure.
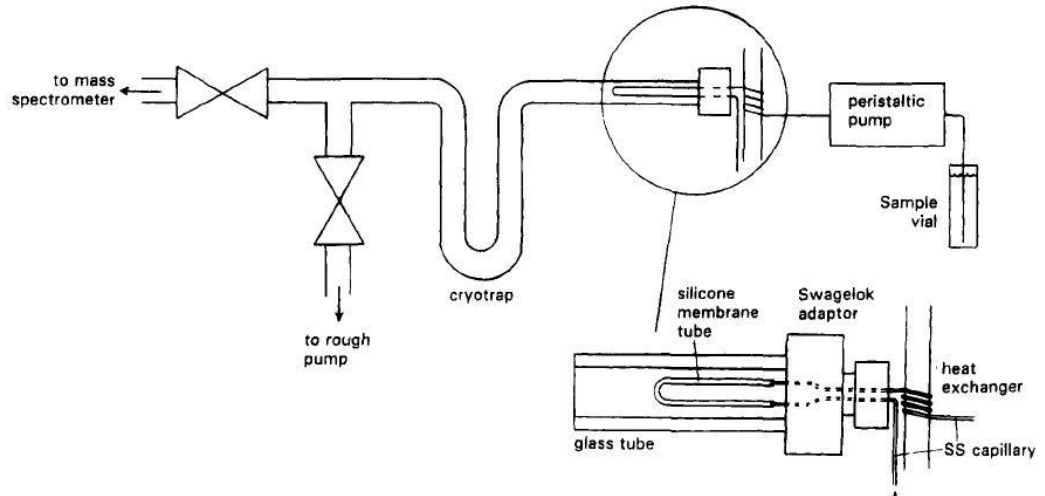
Figure 3: MIMS configuration. Enlarged section shows gas extraction silicone membrane tube. Modified from (KANA et al., 1994).

It's been found that the MIMS instrument responds in a linear way to concentration of the gases, and so a single standard is sufficient (a single point calibration). A water bath with deionized water is held at constant temperature. The gas concentrations in that standard bath are calculated by the Weiss gas solubility equations (WEISS, 1970). Several readings of the standards are made between sets of 15 to 20 samples, to test for instrument drift and allow for drift corrections if needed. Instrument response was measured for masses 28, 29, 30 and 40, the three masses of N_2 and dominant mass for Ar. Concentrations calculated based on the ratio of instrument response for samples: standard. The MIMS, in addition to the liquid nitrogen trap, also has a copper reduction tube maintained at 600 °C to remove oxygen. Oxygen can react with N_2 in the ion source to form NO (EYRE et al., 2002). This is more of a problem for experiments involving repeated measurements in incubations with changing oxygen concentration and for isotope tracer experiments where $^{30}N_2$ measurements are needed, as NO has the same mass as $30N_2$. Still, $^{28}N_2$ measurements are improved by the copper reduction tube. The sample is then pushed past a gas permeable silicon membrane where the vacuum degassed the water sample. Gases then passed through a liquid nitrogen trap to remove water vapor and CO_2. All CO_2 must be eliminated as CO derived from CO_2 has the same mass as N_2. Sample gasses were then drawn into a Balzers Prisma^{TM} quadrupole mass spectrometer.

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Sample concentrations were calculated based on the ratio of instrument response for samples: standard.

Results are given as N2/Ar ratios equivalent to:

$$\frac{N_{2\,sample}}{Ar_{sample}} \equiv \frac{N_{2\,atmosphere} + N_{2\,excess\,air} + N_{2\,denitrifiation}}{Ar_{atmosphere} + Ar_{excess\,air}}$$

(4)

Where $N_{2\,sample}$ and Ar_{sample} are the amounts of dissolved nitrogen and argon in the water sample, respectively. $N_{2\,atmosphere}$ and $Ar_{atmosphere}$ are the concentrations of nitrogen and argon in air saturated water in equilibrium with the atmosphere at a given temperature, salinity and, pressure. $N_{2\,excess\,air}$ and $Ar_{excess\,air}$ are additional amounts of these gases found in the sample attributable to dissolution of air bubbles trapped at the top of the water table (AESCHBACH-HERTIG et al., 1999). $N_{2\,Denitrification}$ is the remaining N_2 gas attributable to denitrification. Determination of excess N_2 attributable to denitrification is dependent on calculating a correct recharge temperature and estimating excess air concentrations.

Sample Collection

Samples were collected in the spring and fall of 2008, to minimize gas exsolution due to higher ambient air temperatures in the summer months. In May 2008 eleven public supply wells and five monitoring wells were sampled. In June 2008 a further six public supply wells were sampled. In October 2008 five public supply wells and one monitoring well were sampled.

In the spring and fall of 2008, the following field parameters were measured with each sample: temperature, pH, specific conductivity and dissolved oxygen using a YSI 556 handheld multi-probe meter. To determine total nitrate and inorganic electron donors, samples for nitrate, anion and cation analysis were collected from each well. 12 ml water for nitrate analysis and 10ml for cation analysis were collected in acid washed (HCl) bottles. Water samples for analysis of nitrate were filtered with Whatman 0.45 micron flow-through filters, field cooled and frozen within 12 hours of collection. Cation samples were field cooled, acidified with HCl to a pH of 3 and refrigerated within 12 hours of collection. Nitrate samples analysis was done by David

Hirschberg of Analytical Services Lab at SUNY Stony Brook's School of Marine and Atmospheric Sciences (SOMAS). Total N-NO$_3^-$ was calculated using a Lachat Instruments FIA-6000 flow injection type automated analyzer. N-NO$_3^-$, Cl$^-$, and SO$_4^{-2}$ data are expressed as mg/l. Nitrate is inclusive of nitrate and nitrite. Anion sample concentrations are reported as the average of three replicate injections. Analytical precision was calculated as the relative standard deviation of three replicate samples. Nitrate precision of one standard deviation is ±2% of sample concentration. Chloride precision to one standard deviation is ± 0.3%. Sulfate precision to one standard deviation is ±3.3%.

Samples were analyzed for Ca^{2+}, Mg $^{2+}$, Na$^+$, Fe^{2+} and Mn^{2+} using a Direct Current Plasma (DCP) in the Geosciences Department at SUNY Stony Brook.   A master standard solution was created using Spex CertiPrep standards. The master solution contained Ca^{2+} and Na$^+$ concentrations of 20ppm, K$^+$ and Mg^{2+} concentrations of 10ppm and Fe and Mn concentrations of 4ppm.   Deionized water was added to make a total solution weight of 120g. An intermediate DCP standard was created by diluting the master standard. The intermediate standard had Ca^{2+} and Na$^+$ concentrations of 10ppm, Mg $^{2+}$and K$^+$ concentrations of 5ppm and Fe^{2+} and Mn^{2+} concentrations of 2ppm.

Resultant concentrations of Fe^{2+} and Mn^{2+} in samples were below detection limit (BDL) of 0.05 ppm for all samples. Standard deviation was calculated from seven samples done in triplicate. The range(R) between the largest and smallest sample observation was calculated as a percent of the average of three readings. The range (R) was then divided by the number of observations (N).

$$\sigma = R / \sqrt{N} \qquad \text{(5)}$$

A common standard deviation was determined by averaging each individual σ and multiplying by 1/k, where k is the total number of samples. Table 1 gives standard deviation for cation analysis.

$$\sigma = \frac{1}{k}\left(\frac{R_1}{\sqrt{N_1}} + \frac{R_2}{\sqrt{N_2}} + \ldots \frac{R_n}{\sqrt{N_n}}\right)$$

(6)

Table 1 Precision of cation analysis. One standard deviation is equivalent to ± percentage given for each ion.

Ion	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe	Mn
% st. dev	1.8	1.4	1.2	3.3	BDL	BDL

Dissolved gas samples were collected in Labco Exetainer® vials with gas impermeable screw cap, dimensions of 101x15.5mm, 12ml volume. Nitrogen and argon gas concentrations were analyzed using a membrane inlet mass spectrometer (MIMS) at masses 28 and 40 respectively. Analytical accuracy for MIMS analysis was taken as the standard deviation for eight replicate injections of a standard at 10^oC, 0ppt salinity. A comparison of these injections with theoretical concentration determined from (WEISS, 1970) solubility equations give percent error for N_2 of $\pm 0.4\%$ and percent error for N_2/Ar of $\pm 0.1\%$. Standard deviation for N_2/Ar ratio is 0.025. Standard deviation for N_2 concentration is ± 1.77 µM/l, or 0.05ppm $N-NO_3^-$.

During the fall of 2008, procedures for *s*ample collection of dissolved gases, nitrate, anions, cations and field parameters are identical to spring sampling period. Additionally, samples for analysis of dissolved organic carbon (DOC) were collected using the following technique. Glass bottles with plastic screw caps were acid washed (HCl) for 48 hours. Glass bottles were then rinsed, dried, wrapped in aluminum foil and heated to 400^oC for 24 hours to burn off any excess organic carbon. In the field samples were collected directly into the filtering syringe, filtered with Whatman 0.45 micron flow-through filters and field cooled. Samples were then acidified to a pH of 2 or less and refrigerated within 12 hours of collection. DOC analysis was done by David Hirschberg of Analytical Services Lab at SUNY Stony Brook's School of Marine and Atmospheric Sciences (SOMAS) on a Shimadzu TOC-5000. Samples are oxidized at high temperature (900° C) using CO_2 free (zero) air as the oxidant. A non-dispersive infrared detector (NDIR) measures the

evolved CO_2 to determine DOC content. Standard solutions are prepared by mixing deionized water with potassium hydrogen phthalate to equal 1, 2 and 3ppm carbon (C), plus a blank. Precision is the standard deviation of three replicate injections of an intermediate standard. The per cent coefficient of the mean is ± 5% for any run.

Site Description

In Northport two types of wells were sampled; public supply wells owned by the Suffolk County Water Authority (SCWA) and observation monitoring wells managed by the United States Geological Survey (USGS). Seventeen SCWA wells and five USGS wells were sampled in the spring of 2008. Five SCWA and one USGS wells were sampled in the fall of 2008. Tables 2 and 3 list well locations and aquifer formation for samples taken during this study.

Table 2 Municipal Supply Well Information: Street location, depth and formation completion.

Location	Identification #	Depth (ft)	Formation
Waterside Rd #2	S-56133	NA	Upper Glacial
Douglas Ave #1	S-33820	412	Upper Glacial
Church Street #2	S-30762	473	Upper Glacial
Church Street #1	S-23371	NA	Upper Glacial
Reservoir Rd #1	S-11105	514	Upper Glacial
Reservoir Rd #2	S-39536	617	Upper Glacial
Gun Club Rd #1	S-15514	593	Magothy
Gun Club Rd #3	S-25776	584	Magothy
South Spur Rd #2	S-37351	593	Magothy
South Spur Rd #1	S-35939	533	Magothy
South Spur Rd #3	S-53747	446	Magothy
Schuler Ave #1	S-22362	316	Magothy
Carlson Ave #5	S-16129	NA	Magothy
Wayne Ct #1	S-118635	372	Magothy
Flower Hill #2	S-48719	NA	Upper Glacial
Hollywood Ave #1	S-66366	677	Magothy
Woodchuck Hollow Rd #1A	S-119294	603	Upper Glacial

Table 3 United States Geological Services (USGS) Monitoring Well Information: Location, depth, screen length, screen interval and formation completion.

Location (Lat/Long)	S #	Depth (ft)	Screen Length (ft)	Screen Interval (ft)	Formation
40.898987/ -73.321783	S-45212	115	10	102-112	Upper Glacial
40.898431/ -73.329561	S-42681	82	5	75-80	Upper Glacial
	S-46962	61			Upper Glacial
40.891765/ -73.406231	S-45053	125	10	104-114	Upper Glacial
40.875376/ -73.41762	S-46281	68	12	38-50	Upper Glacial

RESULTS

The following tables' list data for field collected parameters (table 4), anions (table 5), cations (table 6) and N_2/Ar concentrations (table 7). For tables, S# refers to the unique county code given by the U.S. Geological Survey to all monitoring and municipal supply wells in Suffolk County. Field data collected using an YSI 556 multi-parameter system. Accuracy for pH ± 0.2, temperature ±0.150C, Dissolved oxygen (DO) ±0.2mg/l and conductivity ±0.1% of the reading. A full inventory of accuracy data is available from YSI at

http://www.instrumart.com/assets/108/W11-556-Multiparameter-System.pdf.

Table 4 Field collected data, values for sample temperature, pH, dissolved oxygen (DO) and specific conductivity.

Well Name	S#	Sampling Date	Temp OC	pH	DO (mg/l)	Conductivity (µS/cm)
USGS						
USGS Monitoring	45212	5/14/2008	13.35	5.66	8.9	384
USGS Monitoring	42681	5/14/2008	13.96	6.25	0.4	441
USGS Monitoring	46962	5/14/2008	11.63	6.04	7.6	352
USGS Monitoring	45053	5/23/2008	12.48	5.93	8.4	289
USGS Monitoring	46281	5/23/2008	12.08	5.99	8.1	322
USGS Monitoring	42681	10/6/2008	14.25	6.02	0.2	252
SCWA Supply						
Waterside #2	56133	5/20/2008	11.1	6.5	7.7	283
Douglas #1	33820	5/20/2008	11.4	6.8	9.5	278
Church St #2	30762	5/20/2008	11.6	5.8	10.0	173
Church St #1	23371	5/20/2008	11.2	5.8	10.6	154
Reservoir #1	11105	5/20/2008	10.9	5.9	10.3	243
Reservoir #2	39536	5/20/2008	12.5	7.0	8.7	130
Gun Club #1	15514	5/20/2008	10.7	6.2	9.4	241
Gun Club #3	25776	5/20/2008	10.7	6.1	9.4	270
South Spur #2	37351	5/20/2008	10.8	5.8	10.9	162
South Spur #1	35939	5/20/2008	10.7	5.9	10.9	207
South Spur #3	53747	5/20/2008	10.9	5.7	11.3	156
Schuler #1	22362	6/11/2008	11.6	5.9	7.5	189
Carlson #5	16129	6/11/2008	10.3	5.4	10.8	79
Wayne Ct #1	118635	6/11/2008	10.8	6.2	10.5	159
Flower Hill #2	48719	6/11/2008	11.0	6.2	9.2	150
Hollywood #1	66366	6/11/2008	10.7	5.9	9.9	693
Woodchuck Hollow #1A	119294	6/11/2008	10.8	5.8	10.6	169
Gun Club #1	15514	10/27/2008	10.6	6.1	9.5	278
Waterside #2	56133	10/27/2008	11.0	6.2	8.3	293
Reservoir #2	39536	10/27/2008	11.1	5.5	10.9	236
Douglas #1	33820	10/27/2008	11.3	6.5	6.3	294
South Spur #3	53747	10/27/2008	10.7	5.4	11.3	182

Table 5 Dissolved Organic Carbon, Nitrate, Sulfate and Chloride data. Nitrate is inclusive of

nitrite and nitrate (NO_3^- + NO_2).

Well Name	S#	DOC (mg/l)	N-NO3$^-$ (mg/l)	Cl$^-$ (mg/l)	SO4^{-2} (mg/l)
USGS Monitoring					
USGS Monitoring	45212		10.3	34.1	30.5
USGS Monitoring	42681		0.01	76.1	2.3
USGS Monitoring	46962		4.7	17.8	20.5
USGS Monitoring	45053		7.1	29.8	27.3
USGS Monitoring	46281		9.4	28.2	32.4
USGS Monitoring	42681	2.8	0.3	19.2	3.1
SCWA Supply					
Waterside #2	56133		8.9	24.7	19.8
Douglas #1	33820		5.6	30.1	19.9
Church St #2	30762		10.0	17.5	6.0
Church St #1	23371		6.8	15.9	2.9
Reservoir #1	11105		8.7	28.0	19.7
Reservoir #2	39536		2.0	12.8	4.4
Gun Club #1	15514		8.2	16.2	38.3
Gun Club #3	25776		8.6	16.1	41.3
South Spur #2	37351		6.7	13.5	8.8
South Spur #1	35939		11.0	15.3	29.6
South Spur #3	53747		8.9	14.4	13.7
Schuler #1	22362		5.6	20.6	13.1
Carlson #5	16129		3.3	9.8	1.5
Wayne Ct #1	118635		5.2	9.9	20.9
Flower Hill #2	48719		5.1	14.4	5.7
Hollywood #1	66366		7.4	204.0	15.3
Woodchuck Hollow#1A	119294		6.3	16.2	16.3
Gun Club #1	15514	0.35	7.6	17.4	33.0
Waterside #2	56133	0.49	6.0	20.6	13.7
Reservoir #2	39536	0.36	7.8	24.8	11.8
Douglas #1	33820	0.39	4.7	25.0	14.0
South Spur #3	53747	0.42	7.4	14.0	12.7

Table 6 Concentrations of major cations in groundwater samples in mg/l.

Well Name	S#	Ca+2(mg/l)	Mg+2(mg/l)	Na+(mg/l)	K+(mg/l)
USGS Monitoring					
USGS Monitoring	45212	18.7	7.8	19.6	3.0
USGS Monitoring	42681	21.3	4.1	28.2	3.7
USGS Monitoring	46962	11.8	5.2	12.3	1.6
USGS Monitoring	45053	15.1	6.8	16.2	1.8
USGS Monitoring	46281	20.2	8.0	16.2	2.0
USGS Monitoring	42681	15.3	3.0	24.8	2.9
SCWA Supply					
Waterside #2	56133	22.3	10.0	15.3	1.7
Douglas #1	33820	20.5	8.6	17.2	2.3
Church St #2	30762	12.7	3.7	11.7	1.4
Church St #1	23371	10.3	3.6	10.3	1.2
Reservoir #1	11105	15.4	6.4	13.7	1.5
Reservoir #2	39536	11.1	2.6	8.4	0.9
Gun Club #1	15514	18.8	7.3	11.4	1.4
Gun Club #3	25776	20.3	7.9	12.3	1.5
South Spur #2	37351	10.6	4.4	9.6	1.5
South Spur #1	35939	14.5	6.2	10.7	1.8
South Spur #3	53747	10.1	4.2	9.0	1.5
Schuler #1	22362	10.5	4.9	11.8	1.5
Carlson #5	16129	3.2	1.2	6.3	0.7
Wayne Ct #1	118635	10.1	4.2	8.1	1.0
Flower Hill #2	48719	10.0	4.2	8.6	1.1
Hollywood #1	66366	32.9	15.3	60.0	3.1
Woodchuck Hollow#1A	119294	10.8	4.8	8.4	1.3
Gun Club #1	15514	19.1	7.4	9.7	1.1
Waterside #2	56133	18.8	8.7	12.0	1.6
Reservoir #2	39536	13.2	5.1	11.9	1.3
Douglas #1	33820	18.6	7.8	14.3	1.5
South Spur #3	53747	10.4	4.1	6.8	1.3

Table 7 Dissolved Nitrogen and Argon Concentrations for all well samples.

Well Name	S#	N2 (µM/l)	Ar (µM/l)
USGS Monitoring			
USGS Monitoring	45212	684.3	17.2
USGS Monitoring	42681	840.4	21.3
USGS Monitoring	46962	726.2	18.0
USGS Monitoring	45053	684.4	17.5
USGS Monitoring	46281	691.9	17.5
USGS Monitoring	42681	749.7	18.1
SCWA Supply			
Waterside #2	56133	704.7	17.7
Douglas #1	33820	724.3	17.8
Church St #2	30762	723.3	18.0
Church St #1	23371	731.3	18.1
Reservoir #1	11105	832.1	19.1
Reservoir #2	39536	648.9	17.3
Gun Club #1	15514	729.9	18.2
Gun Club #3	25776	713.0	17.7
South Spur #2	37351	746.7	18.3
South Spur #1	35939	750.7	18.3
South Spur #3	53747	743.8	18.3
Schuler #1	22362	719.6	18.0
Carlson #5	16129	737.3	18.5
Wayne Ct #1	118635	726.6	18.3
Flower Hill #2	48719	734.8	18.1
Hollywood #1	66366	722.1	17.9
Woodchuck Hollow#1A	119294	727.5	18.2
Gun Club #1	15514	704.9	17.6
Waterside #2	56133	653.9	16.5
Reservoir #2	39536	703.0	17.5
Douglas #1	33820	718.4	17.5
South Spur #3	53747	727.8	18.0

pH

Heterotrophic denitrifying bacteria prefer a pH range from 5.5 to 8.0 (Rivett et al., 2008). In groundwater with strongly acidic pH, denitrification can be arrested at the nitrite (NO_2^-) or nitrous oxide (N_2O) stage. Extremely basic pH will promote ammonia volatilization of NH_4^+ during transport to the water table (Porter, 1980). The New York Department of Environmental Conservation reports annual precipitation pH values for Eisenhower Park, East Meadow, NY. Briefly, samples are collected weekly from a hyetometer apparatus. Samples are analyzed using a Fisher Accumet Model 825 MP/mV Meter, with 6.00 and 3.00 pH standards. Weighted averages of weekly sample results are calculated using the following equation:

$$C = \frac{\sum_{i=1}^{n}(P_i * C_i)}{\sum_{i=1}^{n} P_i}$$

(7)

Where C is weighted average, P_i is precipitation (inches), and C_i is concentration.

Table 8 gives the annual precipitation in inches and the average pH for annual precipitation at Eisenhower Park from 2000 to 2007.

Year	Precip. (in)	pH
2000	42.98	4.47
2001	33.89	4.40
2002	46.63	4.56
2003	50.06	4.55
2004	42.77	4.51
2005	49.63	4.63
2006	60.04	4.57
2007	53.23	4.55

In this study, the pH range for water samples from supply wells is 5.4 to 7.0, and for monitoring wells the pH ranges from 5.6 to 6.3.

Recharging groundwater pH is likely controlled by a combination of precipitation pH and soil pH. (BAILEY et al., 2005) found that continual acid rain deposition lowers soil pH at increasingly deeper soil horizons with time. Older groundwater, in excess of 70 years, is expected to have higher pH values as it infiltrated before the onset of acid rain and subsequent

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acidification of soil. Given the fast travel times of Long Island groundwater (~1ft/day), water currently pumped from Northport supply wells is not in excess of 50 years in age(BUXTON and MODICA, 1992) and therefore should have decreased pH due to acid rain precipitation. pH measurements from our samples are slightly elevated in relation to both precipitation pH and average groundwater pH. Average pH in USGS monitoring well samples is 5.98. Average pH in SCWA municipal supply well samples is 6.02.

Conductivity

Dissolved gas solubility is significantly affected by sample salinity (WEISS, 1970). Specific conductivity is a measurement of the sample's ability to conduct an electric current. This value is measured and converted to salinity to ensure that groundwater dissolved gas concentrations do not need a salinity correction. Specific conductivity measurements range from 79 μs/cm to 93 μs/cm for municipal supply well samples and 252 to 441 μs/cm for monitoring well samples. When results are converted to salinity all values are less than 2ppt.   Salinity correction to dissolved gas solubility is unnecessary for Northport samples.

Dissolved Nitrogen

For this study Suffolk County Water Authority identified Northport public supply wells which had greater than 10ppm $N-NO_3^-$ within the last two years. Water samples were collected from a selection of these wells. All samples were analyzed for dissolved $N-NO_3^-$ in order to determine total nitrate content and percent of total nitrate denitrified. The samples had from 1.9ppm to 11.0ppm $N-NO_3^-$. Four of five monitoring wells have dissolved $N-NO_3^-$ ranging from 4.7ppm to

10.2ppm. Well S-42681 was sampled twice having N-NO$_3^-$ values of 0.01ppm and 0.025ppm for spring and fall sampling respectively.

Excess N$_2$ Data

The extent of denitrification is the excess nitrogen gas in a sample after solubility and excess air are accounted for. (HEATON and VOGEL, 1981) were the first to recognize apparent dissolved gas super-saturation of groundwater relative to recharge temperature, coining the term 'excess air'. Excess air is now widely recognized as a consequence of recharging water coming into contact with trapped air in pores, fractures or fissures during its downward travel thorough the aquifer (WILSON and MCNEILL, 1997). Evaluation of data based on Equation 8 depends on an accurate determination of groundwater recharge temperature. Recharge temperature acts as a guide for interpreting the amount of excess air in the sample. The amount of atmospheric nitrogen gas in a sample is based on Henry's law solubility.

$$X_i = k_H (T,S)p_i \qquad\qquad\qquad\qquad\qquad\qquad (8)$$

Where X is the concentration of dissolved gas, k$_H$ is Henry's law constant at given temperature and salinity, p is partial pressure of the gas above the solution. The partial pressure of nitrogen in the atmosphere is constant for a given elevation. The elevation of the water table in the recharge area is between 50 and 80 feet above sea level which has a negligible effect on the pressure. For this system the relevant variables are temperature and salinity. In Northport groundwater salinity was less than 2ppt for all samples. Such low salinities will not affect dissolved gas concentrations. Therefore the amount of atmospheric nitrogen and argon dissolved in each sample is dependent only on recharge temperature.

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The temperature recorded in the field is not an exact representation of the groundwater at time of recharge. As the YSI 556 multiparameter system is contained in a flow through chamber outside the well during pumping, the water temperature recorded can be elevated due to ambient air temperature or exposure to sunlight. Field recorded temperatures for supply wells fall within $\pm 1^{\circ}$C of mean annual temperature. Field recorded temperatures from monitoring well samples are one to three degrees higher than mean annual air temperature.

We use mean annual temperature to determine the amount of N_2 and Ar due to atmospheric equilibration. During travel through the vadose zone water temperature is equilibrated with ambient sediment temperature. Sediment temperature is independent of seasonal effects at depth. Thus, the sediment temperature should be very close to the mean annual air temperature which for Islip, NY is 11.0°C. (http://www.weatherbase.com/weather/weather.php3?s=530527&refer=&units=metric)

Previous workers (BOHLKE et al., 2006; HINKLE et al., 2007) have used a N_2/Ar plot to check interpretations of both recharge temperature and excess air. Samples are plotted with N_2 concentration along the x-axis and Ar concentration along the y-axis. Then an air saturated water curve is plotted with excess air amounts (in cubic centimeters of air per liter) given for a relevant temperature range, in our case 8°C to 11°C. Unreasonable recharge temperatures, as interpreted from Figure 4, indicate degassed or cold-room storage contaminated samples. Two samples experienced cold-room storage contamination; municipal supply well Waterside #2 and USGS monitoring well S#42681.
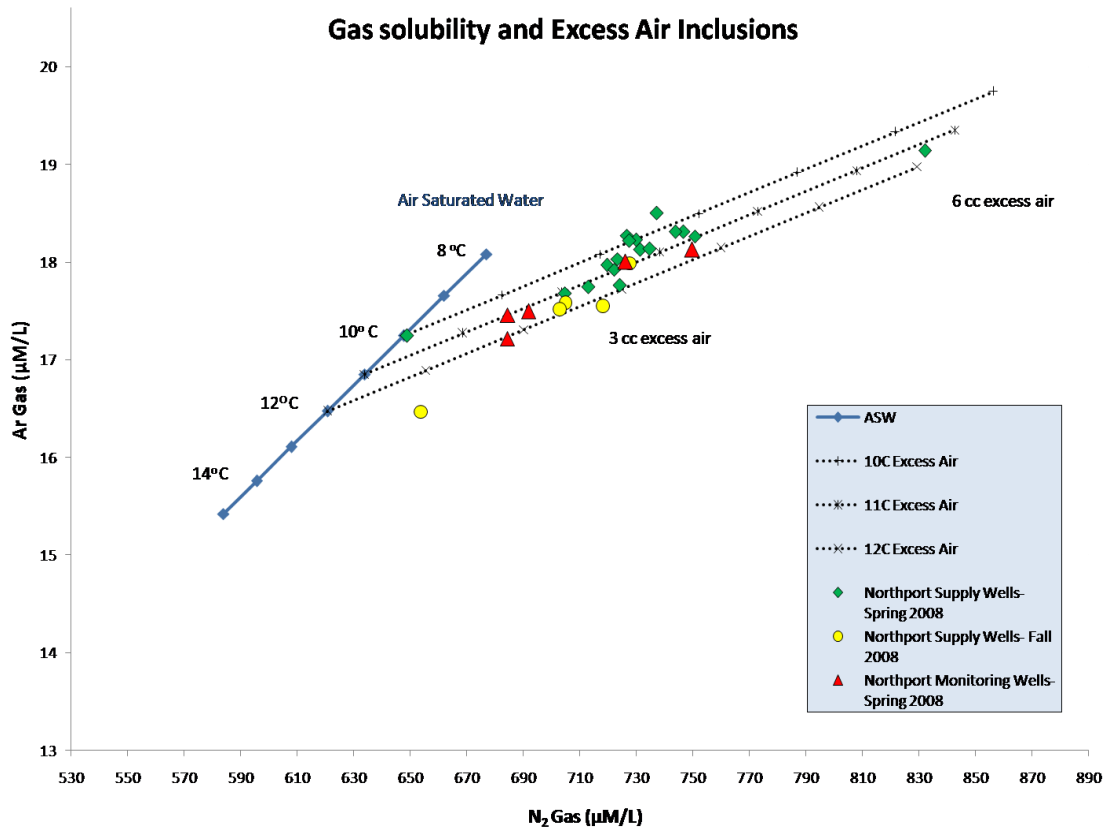
Gas solubility and Excess Air Inclusions

Figure 4 Dissolved Nitrogen gas vs. Argon gas for Northport samples. Air saturated water line represents theoretical gas concentrations at relevant temperatures (8°C-14°C). Excess air curves represent dissolved gas concentrations with excess air entrainment (1cc- 6cc).

Excess air calculations

The largest uncertainty in determining excess N_2 due to denitrification arises from interpretation of excess air ($N_{2\ excess\ air}$). Excess air fractionation can range from complete dissolution of gas bubbles to minimal dissolution of gas bubbles. Without a full suite of noble gas concentrations for each sample it is impossible to determine the precise concentration of N_2 due to excess air (AESCHBACH-HERTIG et al., 1999). Instead the total dissolved concentration of argon in the sample is used to determine the amount of excess air in the sample.

We calculate the uncertainty of excess air concentrations in dissolved gas samples according to the method outlined by Weymann (WEYMANN et al., 2008). If excess air results from complete bubble dissolution then the excess air composition is exactly the same as atmospheric composition (HEATON et al., 1983). For this case we use the ratio of atmospheric nitrogen and argon concentrations.

$$X_{N_2 Excess\ Air} = \left(X_{Ar\ S} - X_{Ar\ EQ}\right) * \frac{X_{N_2\ atm}}{X_{Ar\ atm}}$$

(9)

Where $X_{Ar\ S}$ is the concentration of argon in the sample, $X_{Ar\ EQ}$ is the concentration of argon at atmospheric equilibrium and $N_{2\ atm}$ and Ar_{atm} are the mole fractions of N_2 and Ar in the atmosphere.

If excess air is the result of incomplete bubble dissolution the N_2/Ar is lower due to fractionation. In this case we can calculate the minimum amounts of N_2 and Ar in the sample using the ratio of dissolved N_2 and Ar at atmospheric equilibrium (HOLOCHER et al., 2003).

$$X_{N_2 Excess\ Air} = \left(X_{Ar\ S} - X_{Ar\ EQ}\right) * \frac{X_{N_2 AEQ}}{X_{Ar\ AEQ}}$$

(10)

Where $X_{N2\ AEQ}$ and $X_{Ar\ AEQ}$ are the mole fractions of N_2 and Ar in water at atmospheric equilibrium. Uncertainty arises in determining the exact N_2/Ar ratio of excess air is estimated using the difference between $X_{N2\ Excess\ Air}$ calculated in the using the above equations.

$$U_{N_2 Excess\ Air} = (X_{Ar\ S} - X_{Ar\ EQ}) * ((X_{N_2\ atm} / X_{Ar\ atm}) - (X_{N_2 AEQ} / X_{Ar\ AEQ}))$$

(11)

The following equation was used to determine the amount of excess N_2 due to denitrification.

$$N_{2\ Denitrification} = N_{2\ Sample} - (N_{2\ Atm} + N_{2\ Excess\ air}) \qquad (12)$$

Where $N_{2\ Sample}$ is the concentration of total dissolved nitrogen gas in the sample and $N_{2\ Atm}$, $N_{2\ Excess\ Air}$, $N_{2\ Denitrification}$, are the concentrations of nitrogen in the sample attributed to atmospheric equilibrium, excess air and denitrification, respectively. Minimum and maximum amounts of excess air were used to generate $N_{2\ Denitrification}$. Final $N_{2\ Denitrification}$ was determined to be the average of these two calculations.

The N-NO_3^- denitrified in monitoring well samples ranges from 0.38ppm – 1.07ppm. N-NO_3^- denitrified in supply well samples ranges from 0.25-1.66ppm. Although instrumentation error for MIMS analysis is $\pm$ 0.5%, additional error from interpretation of recharge temperature and excess air exceeds this. Table 9 summarizes the minimum excess air, maximum excess air, N-NO_3^- denitrified and excess air error as determined by equation (11).

Table 9 Denitrification in monitoring and supply wells. Minimum, maximum and error for excess air calculations as determined from equations 9-11. Denitrification determined from equation 12.

Well Name	*S#*	**Min excess air**	**Max excess air**	**Denitrification**	**Excess air error**
USGS Monitoring		**N2 µM/l**	**N2 µM/l**	**N-NO3 (ppm)**	**±N-NO3 (ppm)**
USGS Monitoring	45212	13.79	30.70	0.79	0.12
USGS Monitoring	42681	degassed	degassed	degassed	degassed
USGS Monitoring	46962	43.35	96.48	0.63	0.37
USGS Monitoring	45053	22.84	50.85	0.38	0.20
USGS Monitoring	46281	24.27	54.03	0.53	0.21
USGS Monitoring	42681	48.07	106.99	1.07	0.41
SCWA Supply					
Waterside #2	56133	31.27	69.61	0.57	0.27
Douglas #1	33820	34.22	76.18	0.98	0.29
Church St #2	30762	44.36	98.75	0.50	0.38
Church St #1	23371	47.88	106.58	0.57	0.41
Reservoir #1	11105	86.09	191.63	1.66	0.74
Reservoir #2	39536	14.88	33.12	0.25	0.13
Gun Club #1	15514	51.68	115.05	0.35	0.44
Gun Club #3	25776	33.49	74.56	0.70	0.29
South Spur #2	37351	54.89	122.18	0.68	0.47
South Spur #1	35939	53.12	118.24	0.87	0.46
South Spur #3	53747	54.88	122.16	0.60	0.47
Schuler #1	22362	42.12	93.77	0.50	0.36
Carlson #5	16129	62.02	138.05	0.09	0.53
Wayne Ct #1	118635	53.39	118.84	0.18	0.46
Flower Hill #2	48719	48.31	107.53	0.64	0.41
Hollywood #1	66366	40.32	89.75	0.65	0.35
Woodchuck Hollow #1A	119294	51.50	114.63	0.30	0.44
Gun Club #1	15514	27.40	60.99	0.75	0.24
Waterside #2	56133	degassed	degassed	degassed	degassed
Reservoir #2	39536	24.79	55.18	0.81	0.21
Douglas #1	33820	26.17	58.25	1.18	0.22
South Spur #3	53747	42.84	95.37	0.69	0.37

plots amount of nitrate denitrified against the percentage of nitrate denitrified. Total nitrate

is defined as the sum of denitrified N-NO$_3^-$ and residual N-NO$_3^-$ measured in water samples.

Percent of nitrate denitrified is expressed as:

$$\% N - NO_3^- \ denitrified = \frac{N - NO_3^-{}_{denitrified}}{N - NO_3^-{}_{denitrified} + N - NO_3^-{}_{water}}$$

(13)

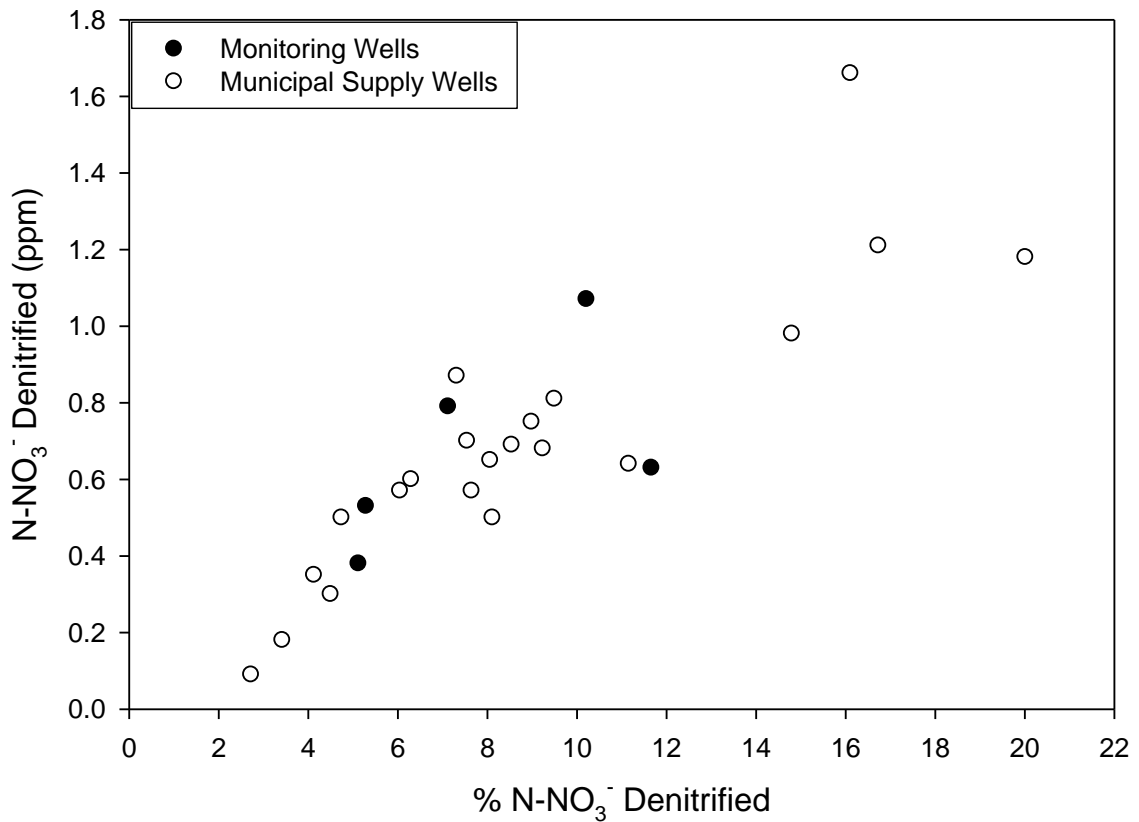Denitrification accounts for less than 2% of total sample nitrate for most samples.

Figure 5 %N-NO3- vs N-NO3- denitrified shows the proportion of total nitrate in the sample that is denitrified.

Total nitrate is defined as the sum of residual N-NO3- in the water sample and average excess N$_2$ Denitrification.

Denitrification accounts for less than 20% of total N-NO$_3^-$ in all samples.

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Dissolved Oxygen Data

Oxygen is the thermodynamically preferred electron acceptor for micro-organism respiration (KOROM and HX, 1992). Denitrification has been shown to occur only when dissolved oxygen falls below a certain level (RIVETT et al., 2008). Thus, dissolved oxygen measurements are useful in determining if denitrification is an important process in groundwater. For example, (RIVETT et al., 2008) reviewed twelve denitrification studies and found denitrification occurred only when dissolved oxygen concentrations were 2 mg/l or less. Dissolved oxygen concentrations in supply well and monitoring well samples were measured using a YSI 556 Multiparameter system attached to a flow through cell.

In Northport monitoring wells four of five samples had dissolved oxygen ranging from 7.5 to 9.0 mg/l. These wells range in depth from 46 to 114 feet. Expected dissolved oxygen concentrations were calculated from air saturated water solubility based on sample temperature and range from 10.2 mg/l to 10.9 mg/l. Based on these calculations water from four of the five sampled monitoring wells was at 70 to 85% of oxygen saturation. Water from well S-42681 had dissolved oxygen content of 0.44 mg/l in the spring and 0.8 mg/l in the fall sampling periods. The water in this well is only at 5% of oxygen saturation.

In municipal supply wells dissolved oxygen concentrations in samples range from 6.3mg/l to 11.3mg/l. Wells range in depth from 316 to 603 feet and are screened in either the Upper Glacial or Magothy aquifer. There is no statistical difference in dissolved oxygen concentrations between the two aquifers. Expected dissolved oxygen measurements from air saturated water calculations range from 10.6mg/l to 11.2mg/l. Therefore, the wells were at 58%-100% oxygen

saturation. Wells that were sampled during the spring and fall have similar dissolved oxygen

concentrations. In Figure 6, N-NO$_3^-$ denitrified is plotted against dissolved oxygen

concentration. Dissolved oxygen in all supply well samples and four of six monitoring well

samples exceed the upper limit of 2mg/l. In all samples N-NO$_3$ denitrified is less than 2 ppm.
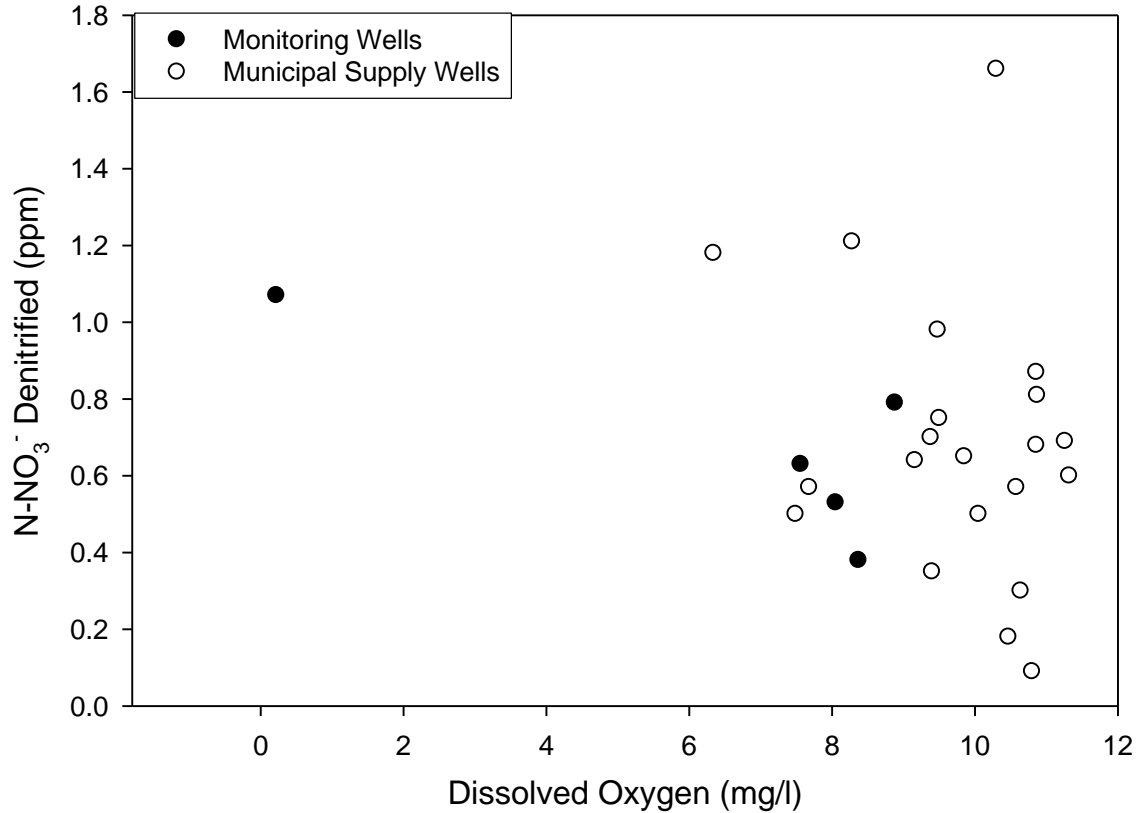

Figure 6 Dissolved Oxygen vs Denitrification in Monitoring and SCWA municipal supply well samples show a correlation between high dissolved oxygen and minimal denitrification.

Electron Donors: Dissolved Organic Carbon, Iron (Fe^{2+}) and Manganese (Mn^{2+})

Electron donors are needed to fuel microbial denitrification. Dissolved organic carbon, reduced iron, manganese and sulfur are the most common electron donors for microbial mediated denitrification (RIVETT et al., 2008). There is some evidence that groundwater containing significant concentrations of Fe^{2+} will contain little to no nitrate (KOROM and HX, 1992). Concentrations of iron and manganese in this study were all below the detection limits of 0.01ppm for the Northport samples.

Dissolved organic carbon is the preferred electron donor for heterotrophic denitrifiers (STARR and GILLHAM, 1993). (CANNAVO et al., 2004) and others related denitrification rate to dissolved organic carbon availability. For this study, samples taken during the fall 2008 were analyzed for dissolved organic carbon (DOC) in order to determine if sufficient electron donors exist to drive the denitrification reaction. Water from one monitoring well and five supply wells were analyzed for dissolved organic carbon. Five supply wells have dissolved organic carbon concentrations ranging from 0.35ppm to 0.5ppm, a typical range for groundwater (LEENHER et al., (1974)).   Rivett et al., (2008) found that DOC levels in most aquifers are less than 5mg/l. Dissolved organic carbon for water from monitoring well S-42681 has a value of 2.80ppm. A summary of dissolved organic carbon concentrations is given in Table 5**.**
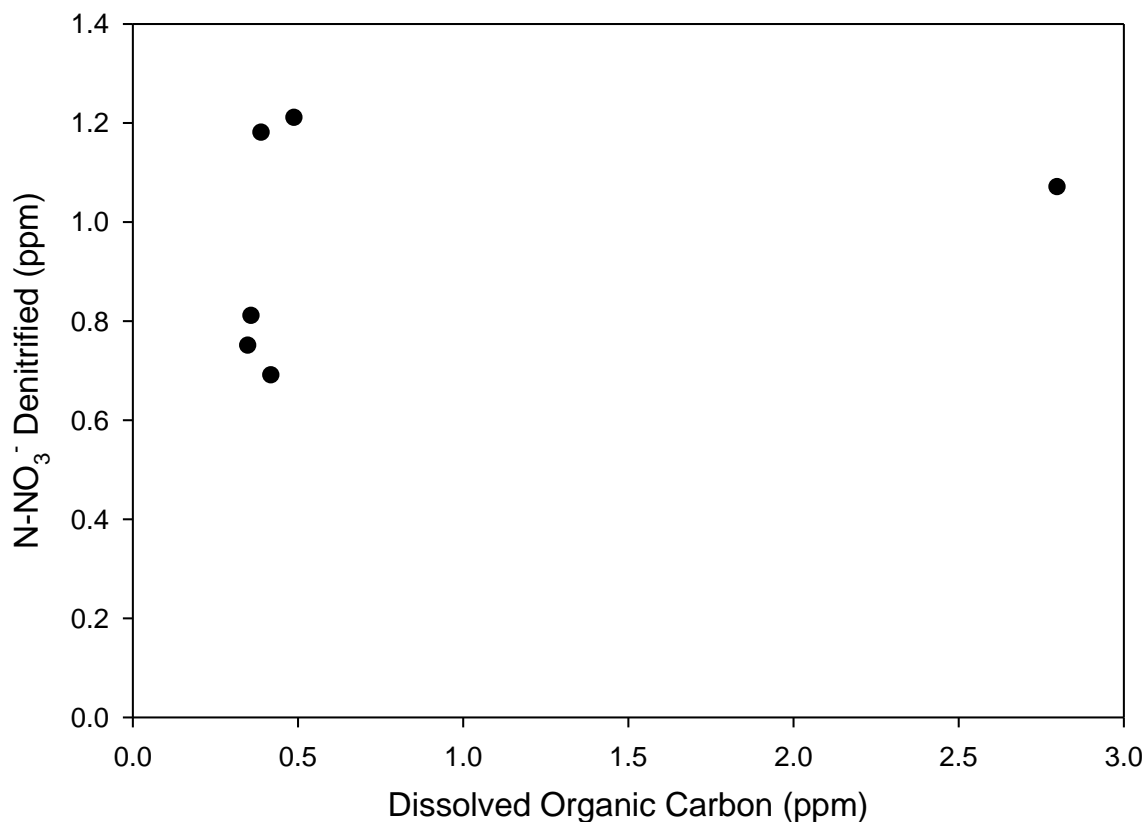
Figure 7 Dissolved organic carbon vs nitrate denitrified for municipal supply wells and monitoring wells

Figure 7 is a plot of dissolved organic carbon against denitrification. All samples contain less than 3ppm dissolved organic carbon. Dissolved organic carbon is first oxidized by dissolved oxygen in the system, and any remaining DOC can possibly fuel denitrification (Rivett et al., 2008).

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{14}$$

This requires 1mg-C/l to convert 2.7mg- O_2/l.   Dissolved oxygen concentrations recorded for these samples are shown in Table 1, and range from 6.3 to 11.2 mg/l for supply well samples.

To deplete dissolved oxygen levels to below 1mg-O_2/l, DOC requirements range from 1.9 to 3.7 mg-C/l. Further DOC is required to fuel denitrification. We observe that DOC concentrations in supply well samples are insufficient to fuel denitrification.

Our results indicate nitrate inputs to Northport groundwater are primarily from on site wastewater treatment effluent with some contributions from fertilizer applications and atmospheric deposition. Groundwater samples contain dissolved oxygen concentrations greater than 4mg/l, dissolved organic carbon concentrations less than 3ppm and excess N_2 equivalent to less than 2ppm N-NO_3^-. The Long Island Sound Nitrogen Influx Reduction Model contains estimates for nitrogen attenuation and denitrification (TEAM et al., 2007) based on groundwater samples taken from beneath a forested parcel. This study sheds new light on the extent of groundwater denitrification in north shore Long Island and is applicable to Long Island nitrogen cycling models.

Discussion

The Long Island Sound Nitrogen Influx Reduction model (TEAM et al., 2007) estimates 50% nitrogen loss from source to receiving body. Of this 50% nitrogen loss, 61% is lost in the vadose zone and 35% is lost in the aquifer. These numbers are drawn from another model done in the coastal plain aquifer of Cape Cod, the Walquiot Bay Nitrogen Loading Model (NLM) (VALIELA et al., 1997; VALIELA et al., 2000). The nitrogen loading model estimated system nitrogen attenuation due to denitrification from a study of denitrification beneath a forested plot within the Walquiot Bay watershed.

The purpose of the study reported here is to determine if aquifer denitrification can account for significant nitrogen loss in the groundwater flow system of Northport, Long Island. Groundwater in Northport has consistently high nitrate concentrations, some greater than 10ppm, and groundwater flow paths that discharge to Long Island Sound. This makes it an excellent site for testing the LISNIR hypothesis that groundwater denitrification accounts for 35% of attenuated nitrogen.

There is no clear consensus on the extent of denitrification in aquifers. Decreases in down gradient nitrate concentrations were observed in Ontario sandy aquifers (STARR and GILLHAM, 1993) and a Maryland sandy aquifer (GREEN et al., 2008). These studies attributed nitrate attenuation to denitrification or some other loss mechanism. Green et al., (2008) used N_2/Ar ratios and ^{15}N and^{18}O isotopes to identify denitrification in California and Nebraska sandy aquifers with low organic matter (0.8-2.3%) and a several meter thick unsaturated zone. Singleton et al., (2007) found extensive denitrification at two sites comprised of unconsolidated

alluvial sands and clays beneath concentrated animal feeding operations in Northern California. Those aquifers had extremely high initial nitrate concentrations, with an average concentration of 98mgL^{-1} N-NO$_3$ near the water table. Nitrate concentrations decreased to less than 3mgL^1 at depths greater than 15m, corresponding to a shift from oxic to hypoxic redox conditions unrelated to sediment type. Seepage from a manure lagoon was the suspected cause of anaerobic conditions and a large contributor of total organic carbon (TOC) driving the denitrification reaction (SINGLETON et al., 2007).

In contrast, a number of authors argue aquifer denitrification is insignificant due to oxygenated groundwater and lack of available electron donors (POSTMA et al., 1991; STARR and GILLHAM, 1993). Khayat et al., (2006) observed minimal denitrification in a shallow sandy aquifer contaminated by septic tank/cesspool plumes in Palestine. ^{15}N-NO$_3^-$ and ^{18}O-NO$_3^-$ isotopes were used to identify sewage and manure contamination(KHAYAT et al., 2006). The majority of samples exhibited no isotopic signature that would indicate denitrification. Conditions in our study are similar to those of Khayat et al., (2006) and the non-denitrifying aquifer studied by Starr and Gillham (1993). In Northport sewage effluent from individual on site wastewater disposal systems is a diffuse non-point source of nitrogen pollution. Aerated soil and thick vadose zones prevent the formation of anaerobic conditions that favor nitrate reduction. *In situ* electron donors like FeS$_2$ are absent and dissolved organic carbon is oxidized prior to entering the water table.

Munster (2004) used major ions in conjunction with well capture zone land use to determine the percent contribution of nitrate from on site wastewater disposal systems, lawn fertilizer and atmospheric deposition in water from Suffolk County Water Authority supply wells

in Northport. Total nitrogen accounted for plant uptake and soil retention prior to determining

groundwater contamination source. Using this method to calculate source contributions of

nitrate, atmospheric deposition can account for 0-20% of total nitrate, fertilizer applications can

account for 0- 40% of total nitrate and on site wastewater disposal systems can account for 10-

50% of total nitrate in well samples.   Five municipal supply wells sampled by Munster (2004)

were also sampled in this study.

Table 10 Nitrate concentrations in this study and (MUNSTER, 2004)with percent contribution from waste water and lawn fertilizer calculated from anion and cation concentrations, estimated nitrate concentrations without nitrogen loss and denitrification calculated from excess N2 using N2/Ar ratios.

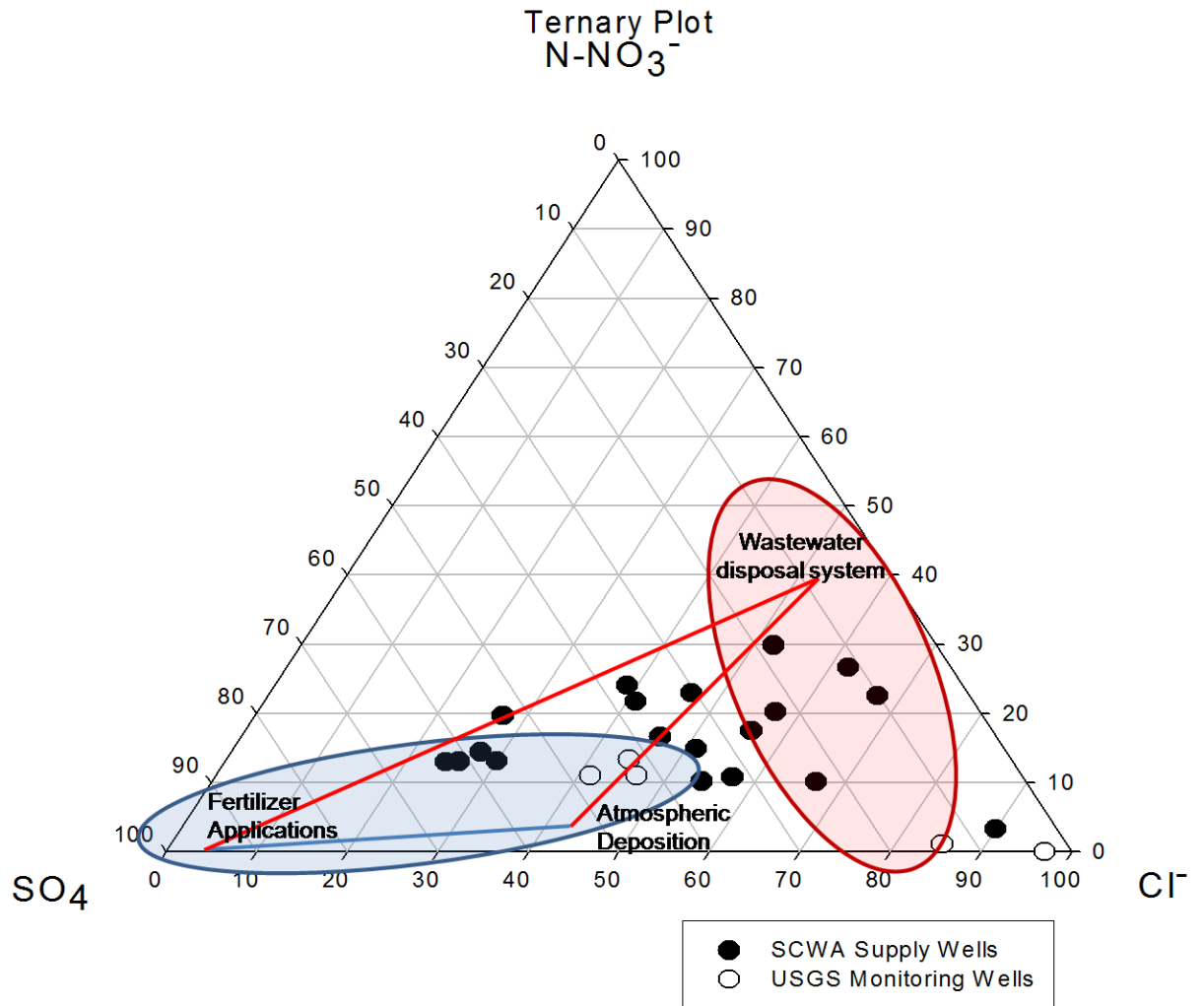| Well	%contribution wastewater disposal systems	%contribution lawn fertilizer	Est. N-NO$_3^-$ (ppm) with no nitrogen loss	Measured N-NO$_3^-$ (mg/l)	Denitrification N-NO$_3^-$ (ppm) from N$_2$/Ar
S#	Munster (2004)	Munster (2004)	Munster (2004)	Munster (2004)	This study
11105	22%	18%	15.1	6.9	0.24
15514	15%	28%	12.7	7.2	0.48
25776	14%	23%	12.7	7.6	0.27
39536	22%	11%	14	7.9	0.34
56133	22%	15%	14.9	7.8	1.49

Table 10 compares the expected amount of denitrification with the measured extent of

denitrification using N$_2$/Ar ratios in groundwater. Percent groundwater sample contribution

from on site wastewater disposal systems and lawn fertilizer applications provides an estimate

of nitrate concentration without nitrate loss. As seen in from measured N-NO$_3^-$ column,

approximately 50% of nitrogen is lost in the system. Finally, denitrification determined from N_2/Ar is given. Measured denitrification in these five wells using excess N_2 concentrations indicates that denitrification can account for less than 10% of the observed nitrogen loss.

Verification of nitrogen inputs for this study was done using the method outlined by Munster (2004). Measured concentrations of $N\text{-}NO_3^-$, SO_4 and Cl^- were plotted in a ternary diagram. Source water for Northport wells is derived from a combination of atmospheric deposition, fertilizer applications and on site wastewater disposal systems. On site wastewater disposal systems have higher concentrations of $N\text{-}NO_3^-$ and Cl^- when compared to soilwater leached through fertilizer applications (MUNSTER, 2004). Samples with low levels of SO_4 indicate older pre-industrialization source water as acid rain produces higher SO_4 concentrations in groundwater.

Figure 8 shows results from anion analysis. All SCWA samples lie either along the soil-water/cesspool mixing line or the atmospheric deposition/cesspool mixing line. This indicates samples contain 20% or greater contributions from on site wastewater disposal systems and/or soilwater. All SCWA wells sampled in this study have medium density housing, 2-10 dwelling units per acre, as the primary land use for the well catchment areas. Three of five monitoring well samples lie along the mixing line for on site wastewater disposal systems/atmospheric deposition, with atmospheric deposition contributing up to 70%. In the remaining two monitoring well samples SO_4^{-2} concentrations are very low. These samples also have $N\text{-}NO_3^-$ concentrations below detection limit of 0.01ppm. Chloride concentrations are high in these samples, suggesting initial on site wastewater disposal system contributions. Although no excess N_2 gas was observed in these samples, it is possible the groundwater underwent reducing

conditions in the unsaturated zone and nitrate was converted to ammonium through

dissimilatory nitrate reduction to ammonium (DNRA). Overall, results suggest similar

contributions of atmospheric deposition, soilwater and on site wastewater disposal systems

found in previous studies (BLEIFUSS et al., 2000; MUNSTER, 2004; MUNSTER, 2008).

Figure 8 Ternary diagram of NO3-, SO4-2, and Cl-. Lines indicate mixing between anion end-members. Ovals depict field where on site wastewater disposal systems (waste water) or fertilizer applications are the primary nitrogen contributors to the sample.

The rate of denitrification is largely independent of nitrate concentration (KOROM et al., 2005) at concentrations greater than 1 mg-N/l (RIVETT et al., 2008). Samples from Northport exhibit nitrate concentrations in excess of 1 mg-N/l (Table 5), indicating that denitrification is possible with respect to electron acceptor concentration. Given the concentration of nitrate in water samples, any denitrification reactions occurring in Northport supply wells are dependent on hypoxic conditions and availability of DOC.
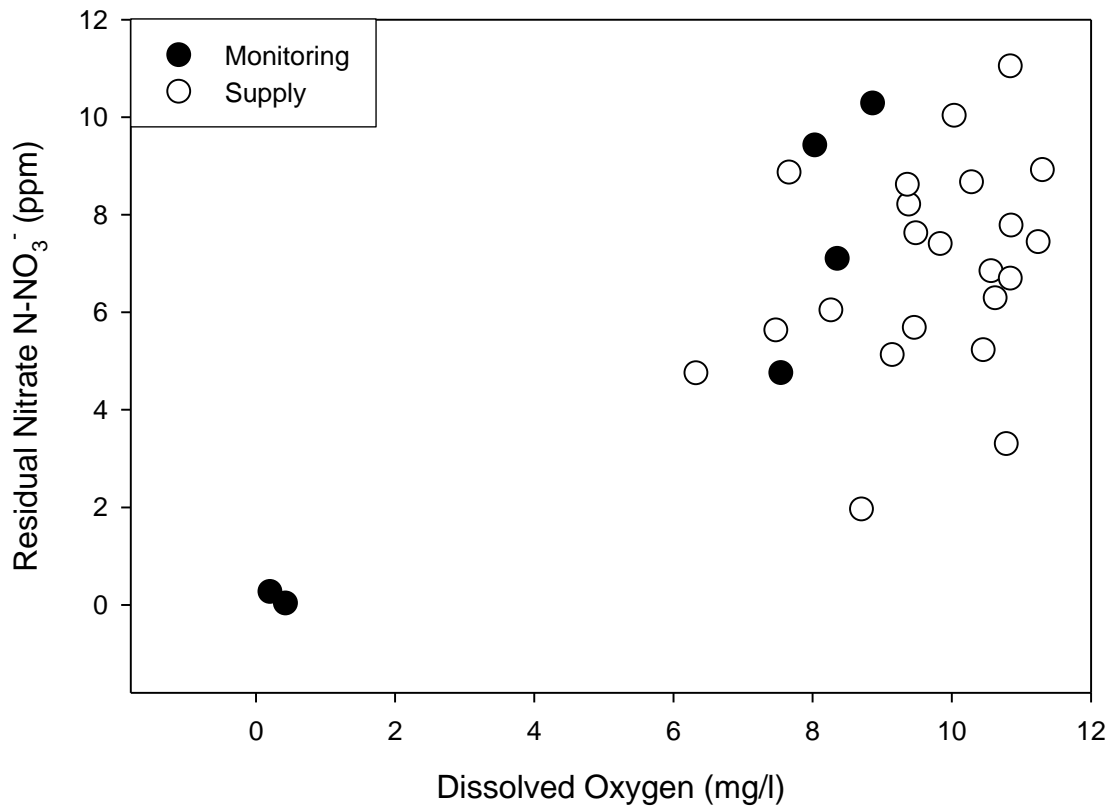
Dissolved Oxygen

Long Island's near surface sandy sediments are well aerated and drained. Oxygen depleting processes such as nitrification are insufficient to exhaust dissolved oxygen supplies (STACKELBERG, 1995). Atmospheric contamination during sample collection is a possible cause of elevated dissolved oxygen concentrations. Oxygen contamination would occur during gas exchange during sample collection. If this occurred, dissolved argon concentrations would reflect ambient air temperature, not average annual temperature of 11°C. Average air temperature for May is 20.5°C (http://lwf.ncdc.noaa.gov/oa/climate/online/ccd/maxtemp.html). Dissolved argon concentrations at equilibrium for 20.5°C should be ~13.9µM/l. Table 7 gives dissolved argon concentrations ranging from 16.5-21.3µM/l in monitoring and municipal supply well samples. As argon concentrations are significantly higher than expected from May ambient temperatures, we find no atmospheric contamination in well samples. Therefore high dissolved oxygen concentrations reflect aquifer condition, not sampling artifacts.

There are a number of possible causes for elevated dissolved oxygen concentrations in aquifers with thick, greater than 50ft thick, vadose zones. Core samples taken in Northport as part of the Town of Huntington Final Remedial Investigation for the East Northport Landfill

(CAMP et al., 2005) indicate much of the Upper Glacial aquifer is locally interbedded with Smithtown Clay. Smithtown clay has an estimated horizontal hydraulic conductivity of <25 ft/day and vertical hydraulic conductivity of 0.0029 ft/day (BUXTON and SMOLENSKY, 1999). These values are much lower than horizontal hydraulic conductivity of 20-200 ft/day and vertical hydraulic conductivity of 0.8 – 1.05 ft/day estimates for the Upper Glacial aquifer in Northport (BUXTON and SMOLENSKY, 1999; CAMP et al., 2005). A comparison of dissolved oxygen concentrations and nitrate denitrified for Northport samples shows a correlation between high oxygen levels and no denitrification (Figure 6). Two monitoring well samples contained less than 1 mgL^{-1} dissolved oxygen but did not contain excess N_2. These samples contained less than 0.01 N-NO$_3^-$ and low levels of SO$_4$ indicating possible reducing conditions in the aquifer or unsaturated zone. Figure 9 compares dissolved oxygen and residual nitrate confirms that wells with high oxygen also contain high concentrations of nitrate. Monitoring and supply well samples contained near saturation amounts of dissolved oxygen, not as artifacts of sampling, but as part of oxidizing conditions that favor nitrification and do not allow for 35% nitrogen loss in the aquifer.

Dissolved Oxygen vs Residual Nitrate

Figure 9 Dissolved oxygen vs. residual nitrate. Residual nitrate defined as nitrate contained in well samples.

Samples with high dissolved oxygen contain residual nitrate ranging from 2-12 ppm.

Rivett et al., (2008) reviewed the concentrations of dissolved oxygen in groundwater

denitrification studies all over the United States. Nitrogen input sources vary from agricultural

fertilizer to septic system plume. Aquifer conditions are unconsolidated glacial or alluvial sands

and clays and include riparian buffer zones in some studies. Table 11 illustrates their findings;

denitrification is not observed where dissolved oxygen concentrations exceed 4 mg-O_2/l. Our

work is in agreement with this. Monitoring well S-42681 has low dissolved oxygen of 0.44 mg-O_2/l, but this does not correspond with an increase in excess N_2.

Table 11 Dissolved oxygen Concentration Threshold for denitrification in a review of studies investigating nitrogen loss in groundwater. Denitrification was observed in groundwater with dissolved oxygen concentration lower than the listed amount. Modified from (RIVETT et al., 2008).

Dissolved Oxygen concentration (mg/l-O2)	Conditions	Reference
4	Agricultural fertilizer plume	Bolke and Denver (1995)
2–3	Agricultural fertilizer plume	Tang and Sakura (2005)
2	Literature survey – varied conditions	Bates and Spalding (1998)
2	Septic waste plume	Gillham (1991)
1.2	Agricultural fertilizer plume	Gallardo and Tase (2005)
1	Agricultural fertilizer plume	Puckett and Cowdery (2002)
1	Agricultural fertilizer plume	Bolke et al. (2002)
1	Landfill plumes	Christensen et al. (2000)
1	Natural (arid zone, Tz30 C)	Vogel et al. (1981)
1	Septic waste plume	DeSimone and Howes (1998)
1	Septic waste plume	Starr and Gillham (1993)
0.2	Tracer injection experiment	Trudell et al. (1986)

Electron Donors

Dissolved oxygen concentrations indicate oxidizing conditions prevent denitrification in the groundwater supplying municipal and monitoring wells tested as part of this study. Where reducing conditions are present, as in monitoring well S-42681, electron donors are the limiting factor in denitrification.   Denitrification electron donors include dissolved organic carbon (DOC), Fe(II), Mn (II), and reduced sulfur compounds. Many studies have investigated the relationship between denitrification and dissolved organic carbon concentration (JACINTHE et al., 2003; STARR

and G_{ILLHAM}, 1993). In a review of denitrification studies, Rivett et al., (2008) suggest electron donor supply is the major factor limiting denitrification in aquifers.

Iron and manganese concentrations were below detection limit for all Northport samples. Based on lack of excess N_2 gas and dissolved oxygen concentrations above cutoffs listed in table 3, iron and manganese are not important electron donors in the Northport groundwater system.

DOC is critically important in denitrification reactions because it is the most commonly available and energetically favorable electron donor.

$$5\ C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 12N_2 + 30CO_2 + 42H_2O \qquad \Delta G = -2670\ kJ/mol\ (S_{TROHM}\ et\ al.,\ 2007)(15)$$

Dissolved organic carbon (DOC) concentrations from five Northport Supply wells range from 0.35ppm to 0.5ppm and one monitoring well has a value of 2.80ppm. Possible sources of DOC in Northport aquifers are septic/cesspool sewage, and solid phase organics in the aquifer body. Because lawns in the watersheds of Northport wells are fertilized primarily with chemical fertilizer not organic manure, lawn fertilizer is not a viable source of DOC. MacQuarrie et al., (2001) effectively modeled septic cesspool plumes using a source value of 82 mg-C/l , but found that DOC is usually oxidized prior to or simultaneously with ammonium in the unsaturated zone and does not act as an electron donor for denitrification in sandy aquifers (M_{ACQUARRIE} et al., 2001). Low DOC concentrations in supply well samples agree with other authors, whose findings suggest that DOC in sewage released from on site wastewater disposal systems in the Northport watersheds is oxidized in the vadose zone before entering the groundwater(M_{ACQUARRIE} and S_{UDICKY}, 2001).

Figure 10 depicts dissolved organic carbon vs N-NO$_3^-$ denitrified and residual N-NO$_3^-$. It is apparent that Northport supply well groundwater contains low DOC, low excess N$_2$ due to denitrification and high concentrations of residual nitrate. (ROBERTSON et al., 1991) studied nitrate concentration and denitrification in a septic plume and found that denitrification was facilitated by high amounts of solid phase organics in the aquifer sediment. The Upper Glacial aquifer is sand dominated with a scarcity of solid phase organics (Buxton and Modica, 1992(BUXTON and MODICA, 1992)). Anaerobic conditions are not easily generated in sand aquifers due to high permeability.   In Northport, aerobic cesspool plumes promote oxidation of DOC before it enters groundwater. Therefore, on site wastewater disposal systems cannot leach sufficient DOC to drive groundwater denitrification.
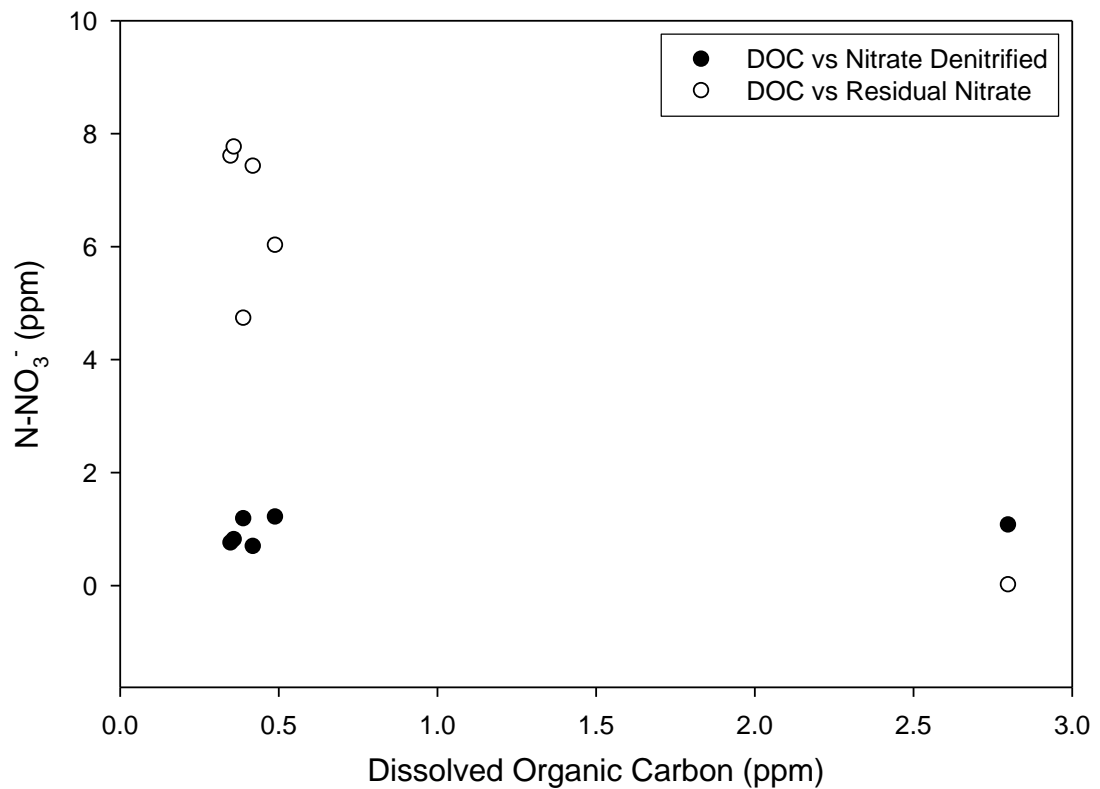
Figure 10 Dissolved Organic Carbon (DOC) vs Residual and denitrified N-NO$_3^-$. DOC and denitrified N-NO$_3^-$ are both less than 2 ppm, which correlates to residual N-NO$_3^-$ greater than 5ppm for Northport supply well samples. One monitoring well was sampled; it contained DOC of 2.8ppm with residual and denitrified N-NO$_3^-$ less than 0.01 ppm.

Isotope and Excess N$_2$ Analysis

In five municipal supply wells concentrations of excess N$_2$ (as N-NO$_3^-$) and residual nitrate determined in this study were combined with nitrogen isotopic composition (^{15}N-NO$_3^-$) determined by Bleifuss (2000) to characterize the extent of denitrification in the system. To do this the ^{15}N signature of initial NO$_3^-$ in these five wells was estimated from percent contribution

of each input; atmospheric deposition, fertilizer applications and on site wastewater disposal systems.

$$^{15}N‰_{Initial} = (\%atmospheric\ deposition * ^{15}N‰_{atmospheric\ deposition}) + (\%wastewater * ^{15}N‰_{wastewater}) + (\%fertilizer\ application * ^{15}N_{fertilizer})$$ (16)

Where %atmospheric deposition, %wastewater and %fertilizer application are the contributions to the capture area groundwater of atmospheric deposition, on site wastewater disposal systems and fertilizer application as determined by anion analysis (MUNSTER, 2004). Table 12 gives the initial isotopic signature of each of the groundwater contribution sources. These isotopic signatures are adapted from previous authors (ARAVENA et al., 1993; BLEIFUSS et al., 2000; FLIPSE and BONNER, 1985). Table 13 gives the percent atmospheric deposition, on site wastewater disposal and fertilizer application contributions for each well and resulting $^{15}N_{initial}$ calculated using equation 16.

Table 12 Initial isotopic signature of groundwater contributions. Signatures are combined to determine the initial ^{15}N value for each of 5 municipal supply samples.

Groundwater Contribution	Initial Isotopic Signature (‰ vs AIR)	Source
Atmospheric Deposition	^{15}N : 2.0‰	Bleifuss, 1998
Wastewater disposal systems	^{15}N : 9.8‰	Aravena *et al. 1993*
Soilwater	^{15}N : 6.0‰	Flipse and Bonner, 1985

Table 13 Percent groundwater contributions and initial ^{15}N value for each municipal well. [15]N values are calculated using Equation (16) and Table 12.

Municipal well S#	%atmospheric deposition	%wastewater disposal systems	%soilwater	Initial 15N‰
56133	40%	40%	20%	5.92‰
33820	40%	40%	20%	5.92‰
11514	27%	33%	40%	6.17‰
25776	0%	50%	50%	7.9‰
53747	30%	30%	40%	5.94‰

The ^{15}N isotope composition of NO_3^- was evaluated in conjunction with excess N_2 and residual NO_3^- for five Northport supply wells. If denitrification is occurring there should be a simultaneous decrease in NO_3^- concentration, increase in N_2 concentration and Rayleigh type isotope fractionation of N and O in the residual nitrate. The Rayleigh type fractionation model uses the initial [15]N , fraction of remaining initial nitrate(f) and the fractionation factor (α) for denitrification to determine the extent of denitrification in a sample.

$$^{15}N_{sample} = (1000 + {}^{15}N_{initial})\, f^{(\alpha-1)} - 1000 \qquad \textbf{(17)}$$

where $\alpha = R_{product}/R_{reacctant}$

The fractionation factor (α) is defined from isotopic ratios of nitrogen, $R = {}^{15}N/{}^{14}N$. The ratio of remaining to initial nitrate in the sample is represented by f. We directly calculated f using excess N_2 measurements from MIMS analysis and remaining NO_3 concentrations.

$$f = X_{NO3}/(X_{NO3} + X_{excess\,N2}) \qquad \textbf{(18)}$$

Denitrification drives the isotopic composition of residual nitrate to higher values of ^{15}N. This enrichment is represented by the isotopic enrichment factor (ε), which is related to the fractionation factor (α) by:

$$\varepsilon = 1000^* (\alpha\text{-}1) \qquad \textbf{(19)}$$

Denitrification usually produces an enrichment factor (ε) ranging from -5 to -40 (HUBNER, 1986). Our analysis indicates enrichment factors (ε) ranging from 0 to -0.2 for the five public supply wells.   Figure 11 depicts nitrate $\delta^{15}N$ vs. fractional extent of denitrification (f). Enrichment lines of -5‰ to -40‰ are given as a guide for typical denitrification plots. Our data points from five Northport supply wells lie below any enrichment lines. Therefore, vadose zone denitrification cannot be the mechanism for 61% unsaturated zone nitrogen loss predicted by the Long Island Sound Nitrogen Influx Reduction (LISNIR) model.
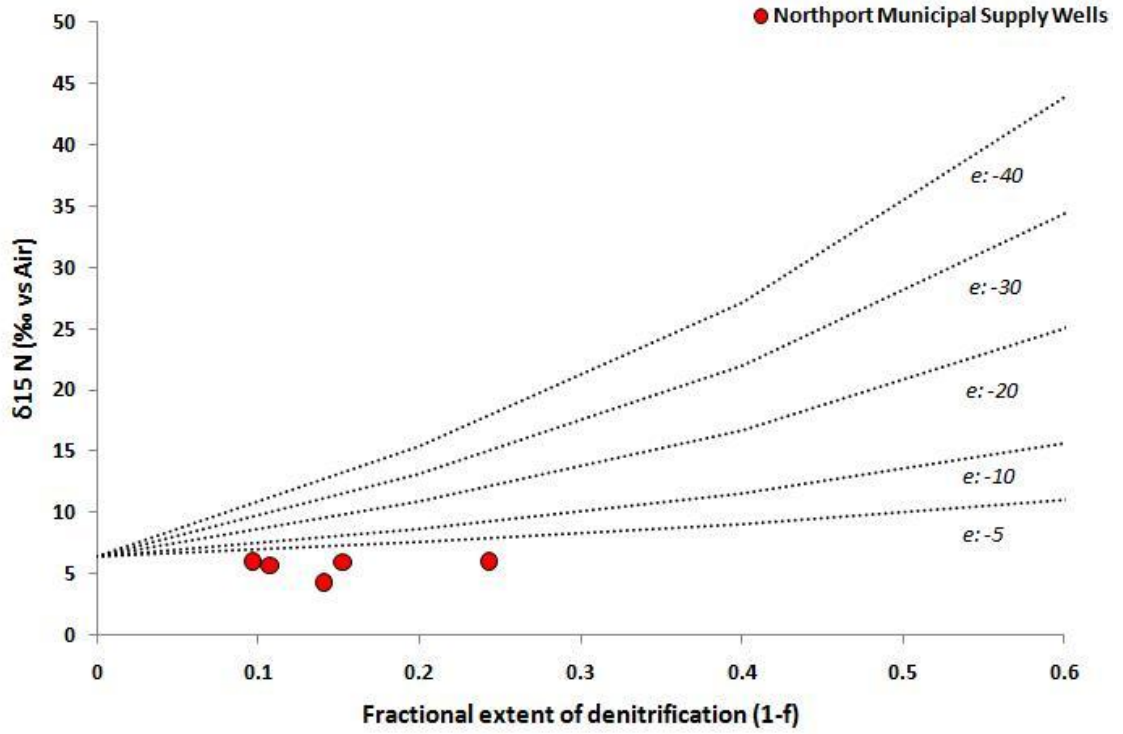
Figure 11 Nitrate δ15N‰ vs fractional extent of denitrification (1-*f*) as determined from excess N$_2$ and residual nitrate in Northport supply well samples.   Enrichment factors (ε) ranging from 0 to -0.2 for five municipal supply wells. δ15N‰ values from (BLEIFUSS et al., 2000). Dashed lines are typical denitrification enrichment factors, -5 to -40 (HUBNER, 1986) with initial δ15N‰ of 6.4‰. The isotope data for Northport groundwater does not plot along enrichment trends due to lack of vadose zone denitrification.

Hypothesis

We examined Northport groundwater for evidence of denitrification in an effort to

determine the mechanism of observed 50% nitrogen loss in the system. We can combine

results from this study with previous investigations (BLEIFUSS et al., 2000; MUNSTER, 2004) to

eliminate denitrification and vadose zone denitrification as primary nitrogen loss mechanisms

for Northport groundwater. There are four possibilities for the observed 50% nitrogen loss in

Northport groundwater system.

1. Ammonia volatilization of ammonium leaving the cesspool

2. Sorption of ammonium onto sediments surrounding the cesspool

3. Denitrification of nitrate in the vadose zone

4. Denitrification of nitrate in the aquifer

Ammonia Volatilization

Ammonia volatilization of ammonium exiting the cesspool was proposed as a method for

nitrogen loss in Northport's aquifers (BLEIFUSS et al., 2000). Ammonification of organic nitrogen

can happen under aerobic or anaerobic conditions (HEFTING et al., 2004), while nitrification

requires a supply of oxygen. Ammonification of dissolved organic nitrogen is the dominant

process in anaerobic septic tanks (PORTER, 1980). Ammonia volatilization occurs when the

ammonium ion is transformed to ammonia gas according to reaction:

$$NH_4^+ \gg NH_{3(g)} + H^+ \tag{20}$$

This reaction requires pH greater than 9. The Long Island Ground Water Pollution Study

(NYSDHS, 1972) found pH in four on site wastewater disposal systems ranged between 6.0 and

6.9, which was similar to pH range of 5.9 to 7.1 found in background wells and downstream observation wells. Upon discharge, the neutral pH of cesspool effluent will quickly equilibrate with ambient soil pH, which is significantly more (JHA, 2007). The pH range of cesspool effluent and Long Island soils does not favor ammonia volatilization. In Cape Cod, MA an aquifer contaminated by on site wastewater disposal systems was studied. Nitrogen transformations were determined from mass balance calculations (DESIMONE and HOWES, 1998). This study found ammonia volatilization accounted for 0.25% of total nitrogen loss in the unsaturated zone. In that study organic and inorganic nitrogen was primarily transformed to ammonium (16%-19%) and nitrate (50%-70%). Given that Northport and Cape Cod, MA have similar coastal plains aquifers, we expect equivalently small amounts of ammonia volatilization at our field site.

Denitrification in Vadose Zone

Vadose zone nitrogen loss is very site specific. The Waquoit Bay Land Margin Ecosystems Research (WBLMER) model to determine nitrogen loads to Waquoit Bay, MA and is used to determine nitrogen loading to Long Island Sound (TEAM et al., 2007). For this model one estimates atmospheric deposition, on site wastewater disposal systems and fertilizer nitrogen inputs then calculates nitrogen loss at each stage of groundwater infiltration, ultimately generating a prediction for nitrogen load to surface water. Inputs are estimated by land use parcels in watersheds and direct measurement of surface body nitrogen concentrations. Outputs are estimated from mass balance losses observed between groundwater near the water table and groundwater entering receiving bodies

WBLMER estimates a vadose zone nitrogen loss of 61%. Therefore 39% of nitrogen entering the vadose zone is predicted to transverse the zone and reach the aquifer. We examined

fractional extent of denitrification, a combination of excess N_2, residual NO_3^- and previous ^{15}N-NO_3^- isotope analysis (BLEIFUSS et al., 2000), and determined that vadose zone denitrification cannot account for vadose zone nitrogen loss estimates of 61%.

Denitrification in Aquifer

While few studies have investigated denitrification in deep public supply wells, previous workers investigating nitrogen transformations in shallower settings have observed a similar vadose zone connection. Pabich et al., (2001) studied the Waquoit Bay watershed aquifers, which has comparable geometry and composition as the aquifer in Northport. They found groundwater DOC concentrations decrease as vadose zone thickness increase (PABICH et al., 2001). Findings indicated groundwater DOC concentrations decrease as recharge area vadose zone thickness increases in sandy coastal plains aquifers. In addition, they hypothesize that within the saturated zone, DOC decreases with increasing depth (PABICH et al., 2001). This is likely due to preferential recharge flow paths that cause a heterogeneous transport of DOC to the saturated zone. Hefting et al., (2004) studied nitrogen transformations in several European riparian settings. They found the main determinant of nitrogen transformation was water table elevation. At water table levels from 0 – 10 cm below surface, denitrification and ammonification processes dominate. At water table level 10 to 30 cm below surface, denitrification was the most significant process. Water table levels deeper than -30cm showed the highest correlation with nitrification rate. Nitrogen cycling trends were not related to climate differences, average soil temperature or annual precipitation.   Since all wells sampled in Northport have depth to water in excess of 5 meters, our results are consistent with the findings of previous authors (HEFTING et al., 2004; PABICH et al., 2001).

Conclusion

We hypothesize that vadose zone thickness controls the low extent of denitrification in Northport. The map in Figure 12 is an overlay of 50 year well catchment areas on vadose zone thickness for the municipal supply wells sampled in this study. Northport SCWA supply well catchment areas are ellipse shaped starting near the Long Island groundwater divide and oriented northward to the supply wells. Vadose zone thickness in the capture zones for municipal supply wells in Northport ranges from 50 to 250 feet.
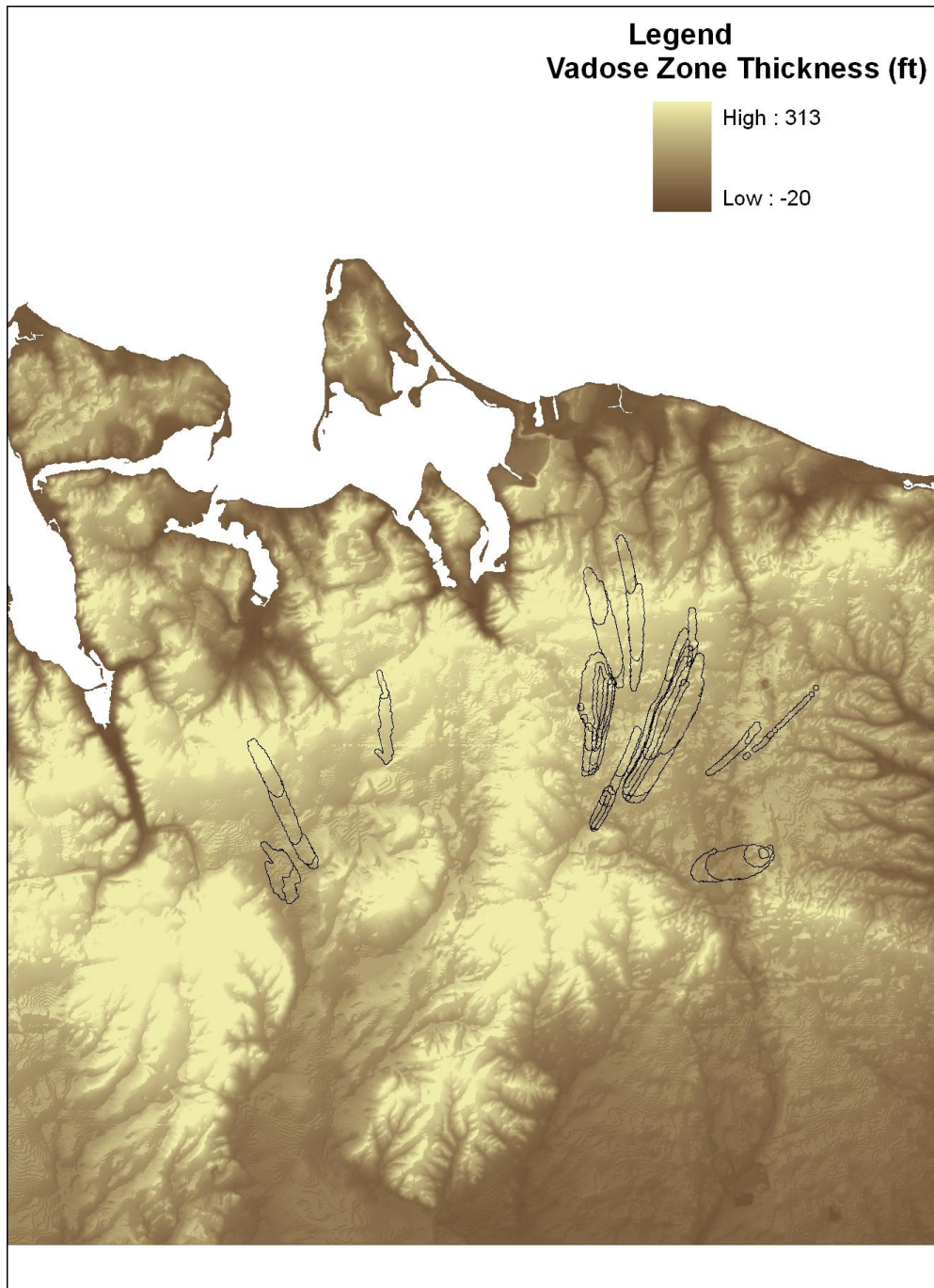
Figure 12 Map of municipal supply well 50 year catchment area over vadose zone thickness for Northport study area. Catchment areas are elliptical, extending south towards the groundwater divide. Vadose zone thickness ranges from 50-250 feet for catchment areas.

Figure 13 depicts a conceptual model of how vadose zone thickness affects nitrogen attenuation in Northport groundwater.   Infiltrating water in the vadose zone is in continual contact with atmospheric gasses, which allows for nitrification of ammonium. High oxygen content mineralizes residual dissolved organic carbon (DOC), producing CO_2. A combination of dissolved oxygen concentrations above 4mg/l and DOC concentrations less than 1mg/l prevent denitrification in Northport groundwater.

Northport: Thick Vadose Zone

Cesspool

CO_2

O_2

Vadose Zone
50 -250 ft

$$CH_2O + O_2 => CO_2 + H_2O$$

$NH_4^+ \leftrightarrow K^+, Na^+, Ca^{2+}, Mg^{2+}$

Cation Exchange
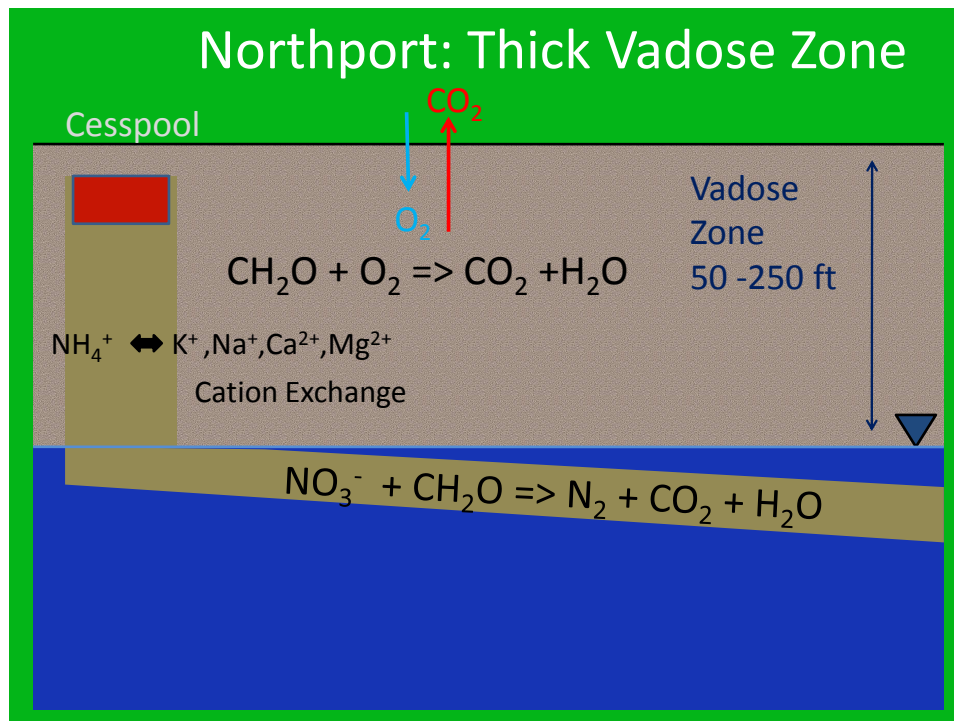
$$NO_3^- + CH_2O => N_2 + CO_2 + H_2O$$

Figure 13 Conceptual model of Northport vadose zone thickness. Catchment area vadose zones range from 50-250 feet thick. A thick unsaturated zone keeps dissolved oxygen content of recharging groundwater near saturation. DOC is oxidized during transport. These conditions prevent aquifer and vadose zone denitrification. Cation exchange is a possible mechanism for nitrogen loss under these conditions.

This study combined with work done by Munster (2004), Bleifuss (2000) and Xu and Hanson (2005) has investigated ammonia volatilization, vadose zone denitrification and groundwater denitrification as possible mechanisms for Northport's observed nitrogen loss. None of these processes can explain the observed 50% nitrogen deficit in Northport groundwater.

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